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TABLE OF CONTENTS

INORGANIC SEMINAR ABSTRACTS

1970-1971

	Page
FOURIER TRANSFORM NMR - Dave McMillin	1
SINGLET OXYGEN - Ray Sweany	4
APPLICATIONS OF MÖSSBAUER SPECTROSCOPY TO HETEROGENEOUS CATALYSIS - Allen Marks	10
A BIT ABOUT SCATTERING - Gary A. Lasby	15
MOLECULAR OXYGEN ADDUCTS OF TRANSITION METAL COMPLEXES - Nelson O'Bryan	16
STUDIES OF ION ASSOCIATION OF $[(n-C_4H_9)_4N][(C_6H_5)_3PCO(II)Br_3]$ AND THE DONOR PROPERTIES OF A FREE RADICAL BASE - Yau-Yan Lim	20
METAL CARBONYLS AS FREE RADICAL SOURCES - Frank L. Slejko	24
STEREOCHEMISTRY OF ORGANOALUMINUM COMPOUNDS AND ION-PAIRS - David J. Brauer	28
HIGH-PRESSURE INFRARED SPECTROSCOPIC STUDIES OF HYDROGEN BONDING - Alan J. Pribula	30
NMR STUDIES OF QUADRUPOLEAR NUCLEI - Robert A. La Rossa	33
CARBON-BONDED BETA-DIKETONE COMPLEXES - Thomas E. Boyd	36
SPECTROSCOPIC AND DIFFRACTION STUDIES OF THE AQUATED PROTON - Arlene R. Mootz	39
PHOTOCHEMICAL SUBSTITUTION OF METAL CARBONYL COMPLEXES - Randolph J. Guschl	41

LANTHANIDE NMR SHIFT REAGENTS - William D. Covey	45
THE NUCLEAR OVERHAUSER EFFECT - Cheryl A. Deckert	49
MASS SPECTROSCOPY OF TRANSITION METAL CARBONYLS - Richard P. Zenger	53
STRUCTURAL STUDIES OF PYRIDINE DIOXIME COMPLEXES OF NI(II) AND NI(IV) - Gordon D. Sproul (Thesis Report)	57
TRANSITION METAL CARBENE COMPLEXES - Michael R. Walczak	59
CHROMIUM (III) PHOTOCHEMISTRY - James Eaton	63
STUDIES ON LEWIS-ACID-BASE ADDUCTS - Thomas O. Maier (Thesis Report)	67
NMR STUDIES OF HALOMETHYLATOBIS(DIMETHYLGLYOXIMATO)- COBALT(III) ADDUCTS - Raymond S. Stewart (Thesis Report)	69
STRUCTURAL AND CHEMICAL INVESTIGATIONS OF SOME ORGANIC AND ORGANOMETALLIC MOLECULES (Thesis Report) - James S. Swanson	71
VIBRATIONAL SPECTRA AND BONDING IN PLATINUM(IV) CYANIDE COMPLEXES (THESIS REPORT) - Mel Memering	74

Dave McMillin

October 27, 1970

Introduction:

Sensitivity in nmr experiments is a vital concern.¹ Many interesting nuclei like ^{13}C are difficult to observe, mainly because of low natural abundance. Using time averaging methods, some success has been achieved. This technique takes advantage of a theorem which states that the entire frequency spectrum can be regenerated from a finite set of appropriately selected points. The results of numerous scans are digitalized, added and then plotted as a single spectrum with a signal to noise (S/N) ratio which is approximately improved by the square root of the number of scans.¹ More recently, it has been shown that pulse techniques in conjunction with time averaging can significantly enhance the sensitivity.² The purpose of this seminar will be to present a simplified discussion of this experiment and to indicate its utility.

Discussion of the Experiment:

Consider polarizing the spins in a static magnetic field $H_0 \hat{z}$ and subsequently introducing a sequence of rf pulses which are spaced at intervals of T sec. along the \hat{x} axis and which are individually described by $2H_1 \cos \omega_1 t$ where each pulse lasts a time τ . The motion of the magnetization describes a regular pattern in which an rf pulse rotates it from an initial position \underline{M}_1 to position \underline{M}_2 after which it begins to relax toward the equilibrium position until its evolution is disturbed by the next rf pulse at position \underline{M}_3 . When a steady state is reached, $\underline{M}_1 = \underline{M}_3$. Under the proper conditions in the rotating reference frame the effective magnetic field approximates $H_1 \hat{x}$ during an rf pulse. This effects a rotation of the magnetization through the angle $\alpha = \gamma H_1 \tau$ toward the x, y plane, establishing a net transverse component for the magnetization. The detector system observes the decay of this transverse component in the time between the pulses. Thus the overall signal or time function that the spectrometer digitalizes and adds successively is the free induction decay (FID) of the magnetization. An appropriate operation by an on-line computer transforms the accumulated FID into the enhanced frequency spectrum of the spin system identical to the usual slow passage absorption signal.

Theory:

It has been shown that the FID of a spin system is the Fourier transform of the slow passage absorption signal.³ The formal proof is complicated, but a rather simplified and intuitive approach indicates the desired result and lends an important physical interpretation.

The Fourier transform of the previously described pulse sequence is a set of discrete frequencies which are sidebands of the carrier frequency ω_1 given by $f_n = \omega_1/2\pi + n/T$ $n = 0, 1, 2, \dots$. If an rf pulse is applied at $t=0$, the y-magnetization for the period $+0 \leq t \leq T$ is given by

$$M_y(t) = M_y(+0) \cos((\beta_1 - \omega_1)t) \exp(-t/T_2) \\ + M_x(+0) \sin((\beta_1 - \omega_1)t) \exp(-t/T)$$

where β_i = Larmor frequency of the set of spins i and $M_x(+0)$ and $M_y(+0)$ are functions of β_i , T , T_1 , T_2 , ω_1 , M_0 , and α .^x The Fourier transform of the periodic signal $M_y(t)$ is a discrete spectrum with frequencies $f = n/T$ ($n = 1, 2, \dots$). With the corresponding coefficients C_n given to a good approximation by

$$C_n = M_0 \frac{T_2}{(\Delta\omega T_2)^2 + 1} \frac{1}{(2T)^{1/2}} f(T_1, T_2, \omega_1, \beta_1, \alpha)$$

where $\Delta\omega = \beta_1 - (\omega_1 + 2\pi/T)$. Thus the line shape is the same in the frequency spectrum of the FID as the usual slow passage absorption signal. The physical analogy which suggests itself is a multi-channel spectrometer. Detailed analysis shows the S/N ratio of the FTS spectrum is enhanced approximately by a factor of $(F/L)^{1/2}$ compared to the usual slow passage signal observed for the same total time. Here F is the total width of the spectrum and L is a typical line width.² Fourier transform spectroscopy (FTS) is particularly advantageous if $T_1 \approx T_2$.

Applications:

The technique has been shown to be very useful for high resolution nmr--any broadening due to deviations from slow passage is avoided.⁴ Systems with large F should be very usefully studied with this method as, for example, ^{13}C systems.⁵ A considerable amount of shift data and coupling constant data for ^{13}C spectra has been accumulated⁶ and interpretation of the spectra has been facilitated. FTS has been shown to be a very efficient method for obtaining ^{13}C nmr in both natural abundance^{5,7} and with small enrichment.⁸ Overhauser effects accompanying proton decoupling yields further enhancement; the resulting simpler spectra aid in the assignment of peaks.⁹ Some systems have long relaxation times, yet short FID because of magnetic field inhomogeneity. Spin echo techniques have yielded much improved results here.^{10,11}

Future:

The future of the method in high resolution nmr seems very bright indeed, particularly for biological systems using ^{13}C . Possible ^{15}N experiments have been suggested.⁷ Applications to inorganic systems are quite feasible. The composition of $\text{Hf}(\text{CN})_5$ in solution could easily have been determined using FTS

as opposed to time averaging.¹² Many heavy metals have isotopes that require high levels of sensitivity. In addition, there are quite promising possibilities in studying transient effects and molecular motion including studies of the Nuclear Overhauser effect and relaxation times for different lines in the same spectrum.¹³

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SINGLET OXYGEN

Ray Sweany

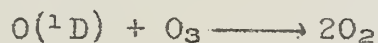
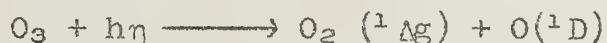
November 5, 1970

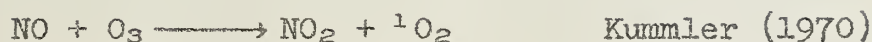
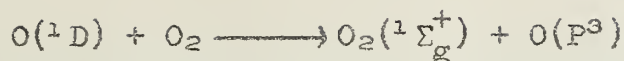
The prediction of a triplet ground state for the oxygen molecule is presented to freshmen as a victory of molecular orbital theory. Recall that two electrons fill the π_g doubly degenerate orbitals so that their spins need not be paired while still obeying the Pauli rule. However, the spins can be paired. Two excited singlet states are possible without disrupting the $KK\sigma_g^2\sigma_u^2\sigma_g^2\pi_u^4\pi_g^2$ configuration; the $^1\Delta_g$ state and the $^1\Sigma_g^+$ state. They are 22.4 kcal and 37.4 kcal above the $^3\Sigma_g^-$ ground state, respectively. Recently, $O_2(^1\Delta_g)$ has drawn particular attention because:

- it often reacts differently from the ground state and at an increased rate,
- it has a relatively long lifetime (3.88×10^3 seconds as an unperturbed molecule),
- it is found in the atmosphere,
- it has been linked to photodynamic action, a process which is capable of destroying chemicals essential for life.

Ten years ago a significant presence of singlet oxygen in the atmosphere was discounted. Leighton (1956) reasoned that a direct excitation of oxygen by sunlight cannot create significant concentrations. The transition from $O_2(^3\Sigma_g^-)$ to $O_2(^1\Delta_g)$ or $^1\Sigma_g^+$ is forbidden by the necessity of a spin change. Ignoring the problem of spin, the transition still must occur by a magnetic dipole mechanism. This type of mechanism results in significantly smaller transition probabilities than electric dipole mechanisms. Leighton failed to realize that, once formed, spontaneous relaxation of the singlet states is as improbable as was their formation. Also, other non-radiative processes are occurring which avoid the necessity of making a spin transition.

While direct excitation can occur, it is exceedingly improbable. The Einstein coefficient for spontaneous emission, A, equals $.085 \text{ sec}^{-1}$ and $.000258 \text{ sec}^{-1}$ for the $^1\Sigma_g^+$ and $^1\Delta_g$ unperturbed molecules. They also give a measure of the probability of energy absorption. Collisions with inert bodies cause these probabilities to increase. The increased probability still can't account for the observed singlet oxygen concentration in the atmosphere. Other sources include:





photosensitization (to be dealt with later).

Rocket soundings in the upper stratosphere have detected maxima for both singlet states at 45 km.

$$[O_2(^1\Delta_g)]_{\max} = 4 \cdot 10^{10} \text{ molecules/cm}^3 \quad \text{Evans et al (1968)}$$

$$[O_2(^1\Sigma_g^+)]_{\max} = 2 \cdot 10^8 \text{ molecules/cm}^3 \quad \text{Wallace (1968)}$$

Kummler (1969) estimated the ratio of $O_2(^1\Delta_g)/O_3$ in California at $2 \cdot 10^{-8}$.

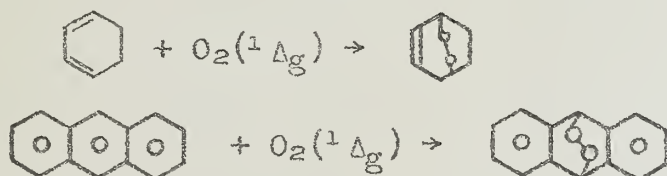
Reactions of singlet oxygen

The electronic configurations of the three lowest states of oxygen can be represented as:

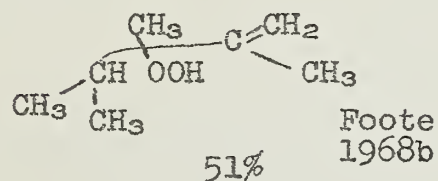
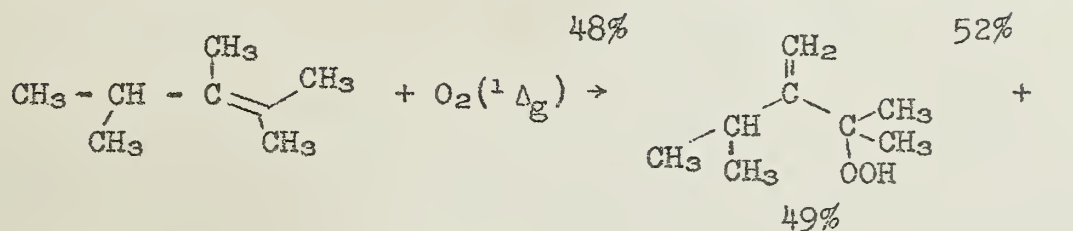
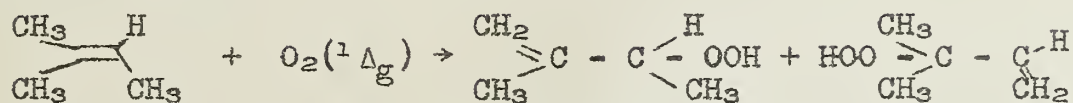
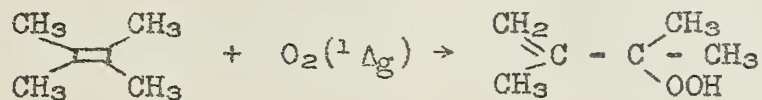


Note the two Σ states are orbitally identical. The unique distribution of electrons in the Δ_g state has been cited as cause for its unique properties. (Foote, 1968a) $O_2(^1\Delta_g)$ reacts with olefins faster, as much as 1000 times faster, than the ground state. Reaction rates of $^1\Sigma_g^+$ with olefins have never been measured. Its rate of reaction with olefins is expected to be as slow as the ground state (Kahn 1969). Typical reactions of $O_2(^1\Delta_g)$ include the following groupings:

a) Reactions with cis dienes to form endoperoxides

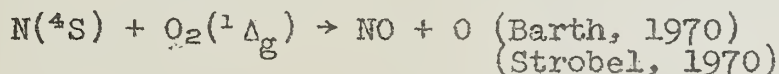
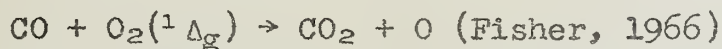


b) Reactions with isolated double bonds to form hydroperoxides



It is not clear to me whether ground state oxygen affects these reactions. Typical oxidations are carried out under conditions which would favor the formation of singlet oxygen; that is, they are performed in the presence of a sensitizer. Light is also necessary. (The significance of these conditions will be dealt with later.)

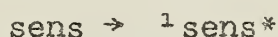
It has been suggested in various places that singlet oxygen plays an important role in atmospheric reactions. The formation of photochemical smog and the enhanced oxidation of atmospheric nitric oxide have been extensively studied. One mechanism put forward suggests it is the reaction of singlet oxygen with olefins which starts a free radical, chain reaction. The hydroperoxide or endoperoxide formed from singlet oxygen would provide the initiating free radicals (Wayne 1969a). The D region of the ionosphere contains more nitric oxide than predicted; the stratosphere contains less carbon monoxide than predicted. Singlet oxygen has been invoked in both situations. It appears that the reactions



are neither fast enough to account for the discrepancies.

Many oxidations of organic materials are worked in the presence of sensitizer molecules under visible or UV light. A common feature of sensitizers is a low lying triplet state. The oxidations promoted by these sensitizers often involve singlet oxygen. A mechanism which has been developed involves:

- a) photoexcitation of the sensitizer to an excited singlet state.



- b) relaxation of the sensitizer to a lower lying triplet state



- c) quenching of the sensitizer triplet



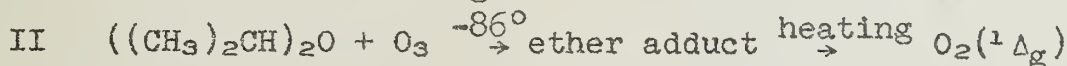
- d) reaction of singlet oxygen with substrate



This mechanism has been shown to be valid in a number of cases, but cannot explain the totality of photo-oxidations (Bourdon, 1969). Photodynamic action is a name given to sensitizer promoted oxidations. A number of tissue components are destroyed in the presence of sensitizer, light and oxygen. Cancer of the skin has been induced by sensitizers. Linking singlet oxygen with sensitizers leads to some interesting hypotheses.

Production of singlet oxygen

For gas phase kinetic study singlet oxygen (${}^1\Delta_g$) is customarily generated by electrodeless radio or microwave discharges (Pitts, 1970). In the discharge, a variety of short lived species are formed as well as singlet oxygen, but they can be removed with reasonable care. In the liquid phase, reactions I and II may be employed and a wide variety of sensitizers are also available.



+ side products (Murray, 1970)

It should be pointed out that these preparations are not totally efficient. Discharges give as much as 10-20% conversion to the singlet state in low pressure flows. Sensitizers may convert up to 70% of the available oxygen to the singlet state. Reaction I produces 70-100% $\text{O}_2({}^1\Delta_g)$; II produces 21%.

Conclusion: Singlet oxygen has recently been discovered as active in some photosensitized oxidations. At the same time, students of the atmosphere began to look for singlet oxygen and discover its role in dynamic atmospheric interactions. As men have been aware of its existence, they have found it being produced in several systems. At this stage, we know only little about what it is doing and what it can do.

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APPLICATIONS OF MÖSSBAUER SPECTROSCOPY TO HETEROGENEOUS CATALYSIS

Allen Marks

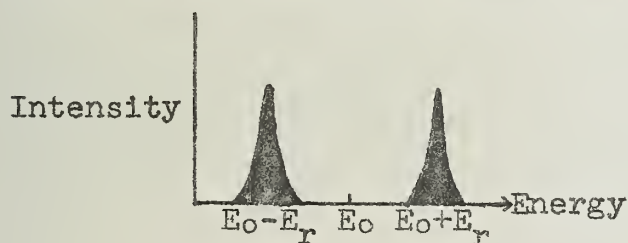
November 10, 1970

Introduction

This seminar will be concerned with some applications of Mössbauer spectroscopy in the study of heterogeneous catalysis.¹

Theory

Mössbauer spectroscopy is based on emission and absorption of γ -rays resulting from transitions between nuclear energy levels. The very small linewidths characteristic of Mössbauer transitions makes the recoil of the nucleus (due to the momentum of a photon) significant. The slight shift in energy prevents an absorbing nucleus from absorbing the emitted γ -rays.



E_0 = Transition Energy

E_r = Recoil Energy

$E_0 - E_r$ = Energy of emitted γ -ray

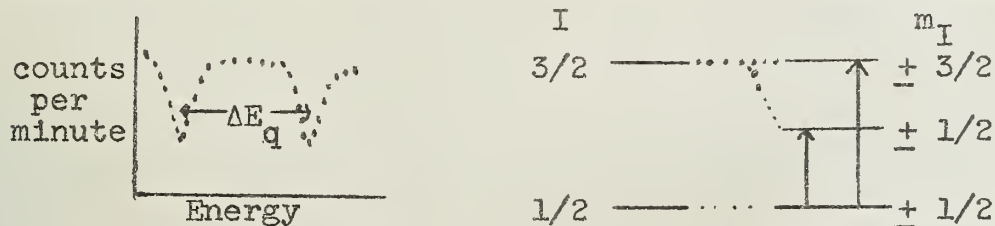
$E_0 + E_r$ = Energy needed to absorb γ -ray

However, if the nucleus is strongly bound (as in a crystal lattice), the recoiling mass is that of the whole crystal. This reduces the recoil energy to a negligible quantity, allowing absorption of the emitted γ -ray. Obviously, if an atom is weakly bound, it will greatly reduce the amount of absorption. The percent effect is an indication of how many γ -rays are absorbed. It is usually defined as the percent of minimum counts to the baseline. This depends on many factors, one of which is the strength of the bonds holding the atom in place.



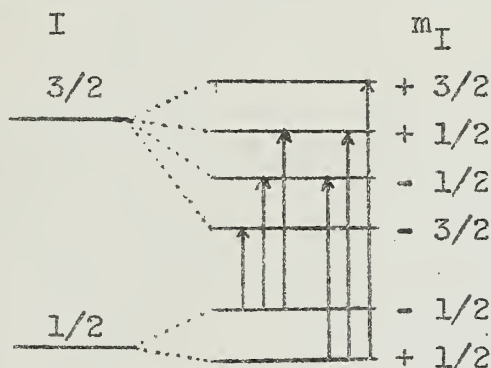
A second shift in the energy of the γ -ray is called the isomer (or chemical) shift. This is due to the finite size of the nucleus which is different at various energy levels. The expanding (or contracting) positive nucleus interacts with the negative electron density at the nucleus, shifting the energy of the transition. This shift is compensated for by moving the absorber relative to the source, using the Doppler shift to make up the energy difference.² Therefore, you frequently see the spectrum plotted versus velocity instead of energy.

If either the ground or excited state of the nucleus is quadrupolar, an interaction between the electric field gradient and quadrupole moment will split the energy into two or more transitions.² For the case of ^{57}Fe in an axially symmetric field:



The excited state ($I=3/2$) is split into two possible projections of the spin (actually two sets of doubly degenerate levels). The ground state is not split. Therefore, two transitions are observed. Their difference is ΔE_q .

If a large enough internal field is present, the interaction of the field with the nuclear magnetic moment will split the degeneracies of the quadrupole doublet. Usually, a strong enough field is present only in ferri-, ferro-, and antiferromagnetic materials.² For ^{57}Fe , we observe six lines. (The $m_I=2$ transitions are too low in intensity to observe.)



Applications

There are many different ways in which Mössbauer spectroscopy can be useful to heterogeneous catalysis. It can be used to obtain the valence states of surface atoms,⁵ to study chemisorption on surfaces,¹¹ the sizes of microcrystals,^{8,9,10} lattice dynamics of surface atoms,^{6,7} structure of multilayer surfaces,¹² and the mechanisms and kinetics of catalyzed reactions.¹³ Only a few of these will be described because of time limitations.

The Mössbauer effect has been used in a study of the changes in a silica gel-alumina catalyst during its preparation.⁵ Four spectra were taken at various stages of the preparation and were interpreted with the aid of temperature studies of the quadrupole splitting. Two iron sites were identified in the spectra of the

reduced catalyst and one in the spectrum of the oxidized catalyst. The oxidized catalyst was found to have only ferric ions while the reduced catalyst was found to have both ferric and ferrous ions. The relative amounts of ferric and ferrous sites are dependent upon the temperature of reduction. Hobson and Campbell⁵ went a step further and deduced the ratio of Fe^{+2} to Fe^{+3} by the area under two of the observed peaks. However, they neglected the possibility of assymetric doublets, therefore, this ratio might be incorrect. This type of experiment will be useful in preparing catalysts commercially. The fact that it is non-destructive makes it possible to take spectra at several different steps.

The Mössbauer effect has been used to study surface states in synthetic zeolites (molecular sieves). Zeolites have a very porous crystal structure and have cations which can be readily exchanged.¹ Gol'danskii, et al.,⁶ have taken Mössbauer spectra of iron exchanged zeolites before and after adsorption of several compounds. It was found that Fe^{+2} was always present, but was mobile or in non-localized positions. The effect of adsorption was to localize the ferrous ions. Delgass, et al.,^{2,7} have taken spectra before and after removal of water from the zeolites. They found that, in the presence of water, some of the Fe^{+2} was effectively in solution and removal of it forced the Fe^{+2} into localized positions. This experiment shows the value of Mössbauer spectroscopy in deducing the structure of the catalyst and its active sites.

Another application of the Mössbauer effect involves the study of finely divided catalysts. When you have small, single-domain particles of magnetically-ordered substances, a phenomenon called superparamagnetism is observed.^{8,9,10} The magnetization vector is held by the anisotropic crystalline field. The energy required for it to go from one direction to another is KV , where K is the anisotropy constant and V is the volume of each particle. There is a relaxation time, t_0 , which indicates how rapidly the magnetization vector changes direction. If this t_0 is much greater than $1/\nu_I$ (where ν_I is the Larmor precession frequency of the nucleus), Zeeman splitting will be observed and the six line hyperfine structure will appear. However, for $t_0 \ll 1/\nu_I$, the particles will be superparamagnetic and only the quadrupole splitting will appear. From Kundig, et al.,⁹ we have

$$\ln(4 \times 10^{-4} K) = 2KV/kT$$

where k is Boltzmann's constant and T is the absolute temperature. A sample of known average particle size is selected such that the particles are mostly superparamagnetic at room temperature; spectra are then taken at progressively lower temperatures. The temperature at which the particles are half-superparamagnetic and half-ferromagnetic can be evaluated. This is the proper value to use in the above equation to get K . From these spectra and K , the average particle size and particle size distribution can be obtained for any other sample of the same material. This can be used below the range of X-ray broadening and is therefore valuable for studying ultrafine particles.

The last application to be discussed involves the study of adsorption complexes.^{1,11} Hobson¹¹ prepared an iron on silica absorber, adsorbed ammonia on it, then removed the ammonia. The spectra taken after each step indicates that the ammonia reduces the amount of ferric ions, but they are partially restored when the ammonia is removed. The explanation given is that there is a net transfer of an electron to Fe^{+3} in the adsorption complex. This also indicates that the Fe^{+3} ions are near or on the surface. This experiment indicates that Mössbauer spectroscopy can be used to study mechanisms of catalyzed reactions by observing changes in the spectra as the reaction proceeds.

Future

There are certain experimental difficulties to be overcome when doing a Mössbauer experiment on surfaces. The major difficulty is that Mössbauer spectra are taken of bulk material. Therefore, surface atoms are only a small percentage of bulk atoms. It is necessary to concentrate the surface atoms. This may be done by using materials with a high surface area or by doping isotopically enriched materials onto the surface. The resolution of some of the peaks is almost impossible because of various types of broadening effects. Computer line shape fits (using Lorentzian line shapes) are usually necessary. To get clean surfaces, a high vacuum is necessary. Vacuums of 10^{-7} to 10^{-9} torr are sometimes necessary.¹⁴ Temperature control introduces absorption and scattering in the cryostat. This reduces the number of counts detected and necessitates longer counting times.

All of the above problems can be overcome and future experiments should become easier as new temperature and pressure techniques are developed. The use of materials enriched in the specific isotope will enhance counting rates and the use of doping will allow study of catalysts that do not contain atoms suitable to the Mössbauer experiment.

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A BIT ABOUT SCATTERING

(Thesis Report)

Gary A. Lasby

November 24, 1970

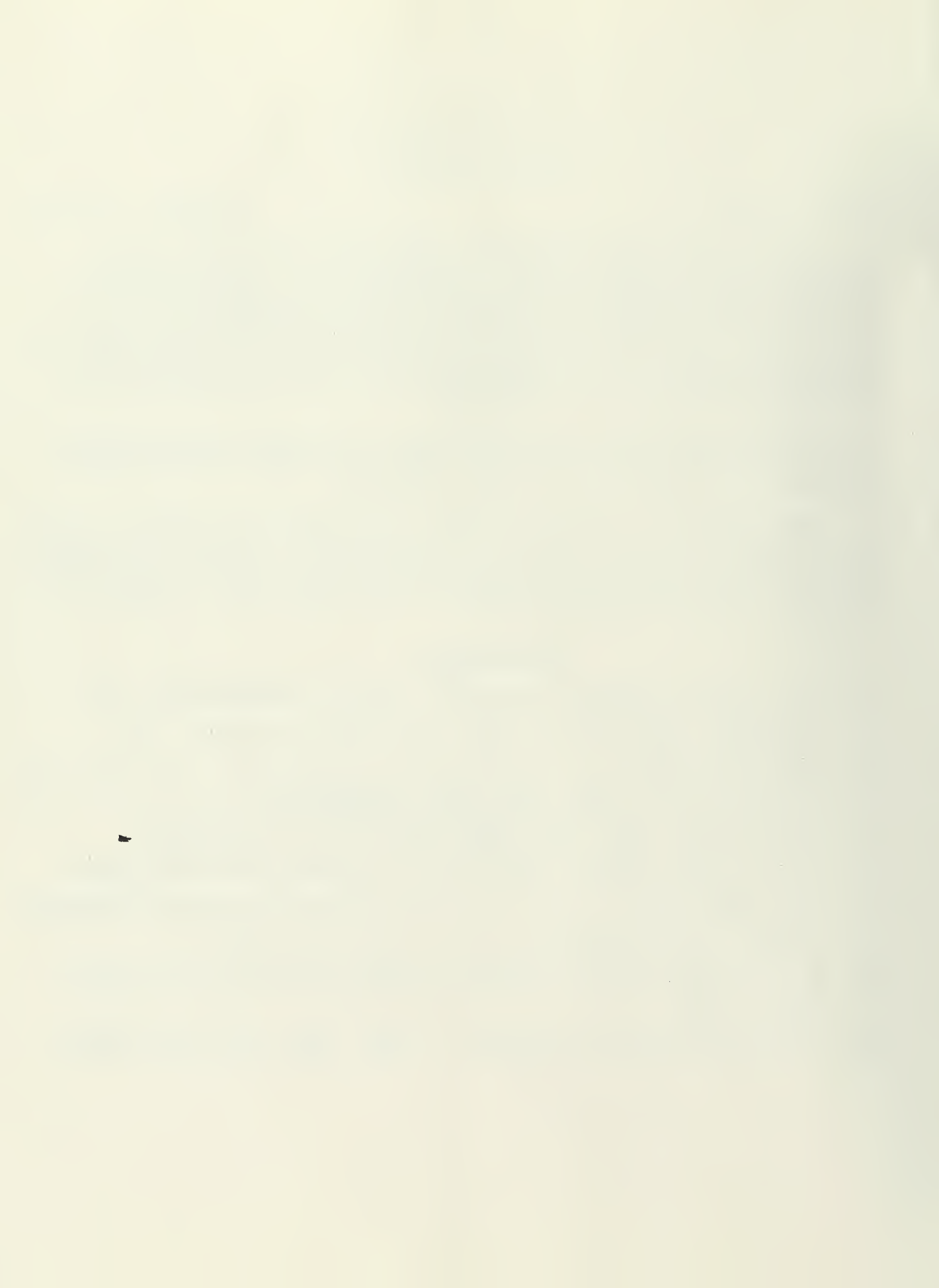
Scattering is the field that deals with the changes that accompany the collision of two or more bodies. The collision can range from a simple elastic collision to a complex inelastic collision where energy of translation is transformed into vibrational or rotational energy or vice versa. In fact, the species that result from the collision may differ from those that were initially present. In short, scattering is the treatment of the fundamental processes of chemistry.

The general theory of scattering is available in many textbooks¹⁻³ and monographs,⁴⁻⁶ while Rapp and Kassal⁷ have reviewed the theory for vibrational energy transfer.

The method of amplitude density functions^{8,9} was used to study the interaction of isotopes of helium with H₂, D₂ and T₂ in a side-ways collision for the interaction potential of Secrest and Gordon¹⁰ and for a strictly repulsive exponential interaction. Results are compared with the colinear case.¹¹

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MOLECULAR OXYGEN ADDUCTS OF TRANSITION METAL COMPLEXES

Nelson O'Bryan

December 8, 1970

Introduction

The study of transition metal complexes which coordinate oxygen has been stimulated by their potentials as models for biological oxygen carriers, particularly hemoglobin. Although dimeric or 2:1 (metal:oxygen) adducts have been known for some time, it has been only in the last decade that synthetic complexes which form 1:1 adducts have been prepared.¹ For purposes of presentation, these complexes are divided into three classes: Vaska's compound and its analogs, cobalt complexes, and the naturally occurring oxygen carriers.

Although the emphasis in this seminar is on structure and bonding in the adducts, a few general remarks about reactions are necessary. Generally, the synthetic complexes bind oxygen simply by bubbling the gas through a solution of the complex. The nature of the solvent is important either in the reaction itself or in stabilizing the adduct. The majority of these complexes bind oxygen reversibly, and are not extremely stable at room temperature. For the reversible adducts, removal of the oxygen can be achieved by heating, applying a vacuum, or bubbling an inert gas through the solution. A few of the complexes will quantitatively bind oxygen in the solid state. Normally, the complex will be completely oxygenated in a matter of seconds to minutes.²

Vaska's Compound and Analogs

The true adducts in this class are characterized by square planar complexes of Ir(I)^{2-9} and $\text{Rh(I)}^{2,6}$. Other Group VIII metals (Pt(O)^{10-13} , Pd(O)^{13} , Ni(O)^{13-15} , Ru(I)^{16}) form oxygen complexes through displacement reactions. The iridium and rhodium adducts are trigonal bipyramidal, whereas the other oxygen complexes are normally square planar. A general characteristic of all these complexes is the presence of some phosphine derivative in two or more of the coordination sites.

All of these adducts are diamagnetic, indicating that the unpaired spins in the π^* orbitals of free oxygen have been paired in the coordinated species. The bound oxygen can be thought of as having paired electrons in one of the π^* orbitals. The oxygen-oxygen bond distance is a sensitive indicator of the strength of the metal-oxygen bond. This bond strength is also influenced by the electron donating ability of the substituent ligands.

For those compounds for which x-ray data are available, the oxygen is symmetrically coordinated to the metal:



$$a \approx 2 \text{ \AA}$$

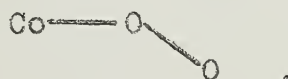
The infrared spectra of these adducts have a strong absorption in the 800-900 cm^{-1} region which can be identified with the oxygen. This frequency has been assigned to the oxygen-oxygen symmetric stretch, but there is some dispute about the validity of this assignment.

The oxygen-oxygen distance (b in the above diagram) varies from 1.30 to 1.66 Å. Thus the bond distances range from that associated with the superoxide ion (1.28 Å) to longer than the bond in the peroxide ion (1.48 Å).

Cobalt Complexes

Square planar complexes of cobalt(II) with some Schiff bases and porphyrins form 1:1 oxygen adducts in the presence of strong Lewis bases. Complexes with N,N'-ethylenebis(3-methoxysalicylideneimine), I,^{18,19,21} and N,N'-ethylenebis(acetylacetonimine), II,^{17,20} have been most widely studied. Both types of adducts exhibit magnetic moments close to the spin only value for one unpaired electron. ESR results^{18,21,23} indicate that this unpaired electron is in a molecular orbital centered on the oxygen; consequently, the adducts might be thought of as Co(III) and O_2^- .

Infrared absorptions associated with the oxygen are quite different in the two complexes, and both are different from those in the Vaska-type compounds. Adducts using ligand I show only a weak absorption around 1140 cm^{-1} . Adducts of II have a very intense band at this same wavelength. The use of magnetic and infrared data support the view that bonding in II is



That for I is still uncertain.

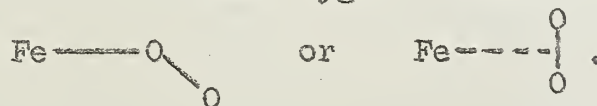
The rate of oxygen absorption and the stability of the adducts are related to the basicity of the base coordinated in the fifth position in these hexacoordinated adducts. Stronger bases give rise to stronger metal-oxygen bonds.

Vitamin B_{12} ²² and related porphyrin cobalt(II) complexes²³ also exhibit the property of reversibly binding oxygen in the presence of bases. These have only one unpaired electron and are similar to the Schiff base complexes.

Hemoglobin and Myoglobin

Hemoglobin and myoglobin contain iron(II) porphyrin groups as the oxygen-bonding centers.^{1,24,25,26} In these molecules, the iron is bound to the protein through the imidazole nitrogen of histidine. The imidazole nitrogen serves a second purpose in stabilizing the adduct through donation of electrons. The protein

furnishes a polar, aprotic medium in which the oxygen can be coordinated. This is necessary since the iron porphyrin complex does not reversibly bind oxygen if removed from the protein. At present, it is not clear if the oxygen is bound



The presence of a second imidazole nitrogen above the oxygen apparently helps to stabilize the adduct although its exact function is not understood.

From similarity of systems, and the necessity for Lewis bases, it is evident that the cobalt systems discussed earlier furnish the best models to describe the reactions and bonding in hemoglobin and myoglobin. An iron(II) bis(dimethylglyoxime) compound²⁷ which forms oxygen adducts in the presence of strong bases has been reported; however, no studies have been done on this system.

Bonding

In general terms, the bonding in these adducts can be described by a donation of electrons from the oxygen π bonding orbital and a concomitant back donation from the metal to an oxygen antibonding orbital. The exact description depends on the metal and the relative orientation of oxygen and metal. The diamagnetism of some and the one unpaired electron in others show that the degeneracy of the π^* orbitals in oxygen is broken, thus ruling out any linear M-O-O bonds. This model with variations successfully accounts for most observed phenomena in the adducts. Thus, the presence of electron donating bases reduces the buildup of positive charge on the metal enabling a greater electron transfer. Since the electrons are going into an antibonding oxygen orbital, this explains the increase of O-O bond length with increasing basicity of the ligands.

Conclusion

So far as is known, the metal of the oxygen adducts must be a low valent transition element from Group VIII. These metals have in common relatively high ionization potentials and are coordinated with polarizable or electron-donating ligands. The ligand and the metal must not be too easily oxidized; otherwise, simple oxidation products of both will result. Acidic protons in both the ligand and solvent must be absent to prevent the formation of hydroxo or peroxo species. A structural condition is that the parent complex have an open coordination site. These rather narrow requirements account for the small number of oxygen adducts discovered.

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Studies of Ion Association of $[(n-C_4H_9)_4N][[(C_6H_5)_3PCo(II)Br_3]$ and the Donor Properties of a Free Radical Base

(Thesis Report)

Yau-Yan Lim

December 15, 1970

I. Solvent Effects on Ion Association

A. Introduction

An ion-pair is formed when two ions combine to form a neutral species where the operative forces of association are mainly electrostatic (i.e., not the same as a polar undissociated molecule). For the last decade or so, the ion-association theory of Fuoss, Denison, and Ramsey^{1,2} has been the main theory employed. Their theory, also known as the sphere-in-continuum theory, is based on the premise that only ions in actual contact are being considered as ion-pairs and no account is given to solute-solvent interaction. They considered that the bulk dielectric constant of the solvent is the only major factor that would affect the nature of ion-pairing and predicted a straight line plot of $\ln K_{as}$ vs. $\frac{1}{\epsilon}$ where K_{as} is the association constant and ϵ the dielectric constant of the solvent. A constant interionic distance in all solvents was assumed. The inherent oversimplifications of their model have led to exceptions to the theory.^{3,4}

In an attempt to obtain new information bearing on the solvent effects on ion association we have initiated studies of the ion-pairing interaction in $[(n-C_4H_9)_4N][[(C_6H_5)_3PCo(II)Br_3]$ in a series of solvents. The results of this study, wherein NMR dipolar or "pseudo-contact" shifts are mainly used, are presented in this seminar.

B. Results

NMR pseudo-contact shifts arise from the dipolar coupling between the magnetic moment of the unpaired electron and the magnetic moment of the nucleus. Reviews of NMR of paramagnetic complexes have appeared.^{5,6} By observing the chemical shifts of the N-methylene proton of the cation of the above complex in various solvents at various concentrations and by using the zinc analog as a diamagnetic reference the association constant and the isotropic paramagnetic shift for a fully paired species were obtained for the solvents o- and m-nitrotoluene, nitrobenzene, and propylene carbonate. The association constants were found to increase with decreasing dielectric constant of the solvent but a plot of $\log_{10} K_{as}$ vs. $\frac{1}{\epsilon}$ did not give a straight line. The observed order of the magnitude of the N-methylene protons paramagnetic resonance shift was found to be

$$\Delta\nu_p(\text{o-nitrotoluene}) \approx \Delta\nu_p(\text{m-nitrotoluene}) \approx \Delta\nu_p(\text{nitrobenzene}) > \Delta\nu_p(\text{propylene carbonate})$$

In spite of the recent reports^{7,8} showing that the isotropic shift of the cationic protons arises both from pseudocontact and from contact contributions, the above order can still be interpreted to mean equal interionic distance (within the limits of experimental error) for the first three solvents (ϵ ranging from 23 to 33) and longer interionic distance in propylene carbonate. It was not possible to evaluate K_{eq} and $\Delta\nu_p$ in chloroform and o-dichlorobenzene because in these low dielectric constant solvents ionic clustering occurs⁹ and the system is no longer adequately described by a 1:1 equilibrium constant.

The isotropic resonance shifts of the N-methylene protons were obtained for a 0.058 M solution in nine different solvents (all found to be chemically inert towards the complex anion by electronic spectral studies) with dielectric constants ranging from 4.65 to 64.2. The $\Delta\nu$ values decrease regularly as ϵ increases for all solvents except those capable of hydrogen-bonding. Explanations will be given of the "abnormal" behavior of the hydrogen-bonding solvents.

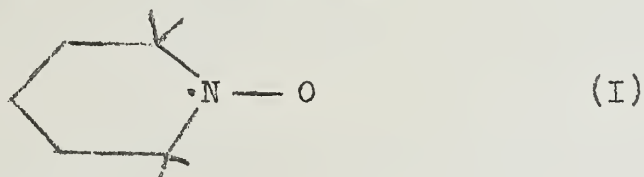
C. Conclusion

This investigation demonstrates the failure of the sphere-in-continuum model to explain ion-pairing phenomenon.

II. Donor Properties of a Free-radical Base

A. Introduction:

Cyclic nitroxide free radicals were first synthesized through the pioneering efforts of some Russian and French workers in the mid-nineteen sixties.¹⁰ The Lewis acid-base adduct that is formed between a nitroxide radical and a diamagnetic acid is paramagnetic and the paramagnetism of the adduct should offer another technique for the study of the nature of Lewis acid-base interaction. The Lewis basicity of the stable free radical, 2,2,6,6-tetramethyl-piperidine-N-oxyl, hereafter designated as (I), was chosen for study.



B. Previous Studies:

The EPR spectrum of I in solution consists of three lines due to the interaction of the unpaired electron (which is delocalized approximately 80% on the nitrogen atom and 20% on the oxygen atom) with the ^{14}N nucleus ($I = 1$). The EPR spectrum is solvent sensitive.¹¹ The increase of the ^{14}N hyperfine splitting constant A_n and the decrease of the g value upon interaction with protic solvents have been proposed to be compatible with the mechanism that the site of interaction is through the oxygen atom. Recently, the free radical (I) was also found to be protonated and complexed with AlX_3 , BX_3 ¹² and GaX_3 ¹³ ($X = \text{halides}$) and the change in A_n and g values were reported. To date, no thermodynamic data for the interaction of the free radical (I) with Lewis acids have been reported.

C. Approach of Present Study:

Calorimetric measurements of the enthalpy of acid-base adduct formation in an "inert" solvent have been coupled with attempts to correlate the enthalpy data with changes in the ^{14}N hyperfine coupling constant and with changes in the $\Delta\nu_{\text{OH}}$ value, the shift in the O-H stretching frequency on adduct formation. It was of interest to see whether the enthalpies could be estimated from the frequency shift correlation^{14,15,16} for the free radical base.

Drago and Wayland proposed in 1965¹⁷ a four parameter enthalpy equation

$$-\Delta H = E_A E_B + C_A C_B \quad (1)$$

where E_A and E_B were originally interpreted as the susceptibility of the acid and base respectively to undergo electrostatic interaction and C_A and C_B as the susceptibility of the acid and base respectively to form covalent bonds. The relative magnitude of the ratio C/E is a good indication of how "soft" or "hard" an acid or base is.¹⁸ The above empirical equation has previously been applied only to systems where no spin-pairing is occurring between the acid and base and it was of great interest to see whether this equation could be applied to the interaction of bis(hexafluoroacetylacetonato)copper(II) with the free radical (I).

D. Results and Discussion:

From calorimetric and EPR data, CCl_4 was found to interact with the free radical. The ΔH values for adducts of the free radical with Hexafluoroisopropanol and Trifluoroethanol agree reasonably well with those predicted from the constant acid enthalpy-frequency shift correlations. However, in the case of phenols, the heats measured in cyclohexane are considerably greater than those predicted from the frequency shifts. The reasons for this are not clear at present. Even though the free radical donor does not fall on the constant acid plots, a constant base plot does exist.¹⁹ From the constant base plot, the enthalpy of 1:1 adduct formation in cyclohexane can be predicted.

The plot of A_N vs. $\Delta\nu_{\text{OH}}$ demonstrates that as the strength of the hydrogen bonding interaction increases, the hyperfine splitting constant A_N also increases. Since A_N is nearly isotropic and the isotropic coupling constant is a direct measure of the unpaired electron density at the nitrogen nucleus, the increased value of A_N with extent of interaction supports coordination to a m.o. which is largely a lone pair oxygen orbital.

Reliable C and E numbers of the base could be obtained by including the $\text{Ca}(\text{hfac})_2$ heat in the solution of equation (1), indicating that the Drago-Wayland equation can be applied to a system where the unpaired electron in $\text{Cu}(\text{hfac})_2$ was found to interact with the unpaired electron of the free radical base. The C/E value of the base (≈ 6) indicates that it is a "softer" base than ethyl acetate, acetone, pyridine-N-oxide and some other diamagnetic oxygen donors.

The result of a cryomagnetic study indicates that the 1:1 adduct of $\text{Cu}(\text{hfac})_2$ with the free radical is antiferromagnetic, but the field dependence of the magnetic susceptibility value in the solution state shows that it is also ferromagnetic. The problems of diamagnetic correction to the observed magnetic susceptibility and the possible mechanisms of spin-spin interaction in this system are discussed.

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METAL CARBONYLS AS FREE RADICAL SOURCES

Frank L. Slejko

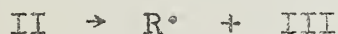
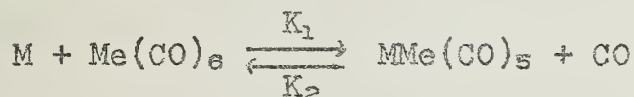
January 5, 1971

Introduction

Although there are several examples in the literature where transition metal complexes act as free radical scavengers, there are few examples where transition metal complexes generate free radicals in solution. Photochemical reactions are usually implicated in these latter cases.¹ This seminar will focus on some reactions of metal carbonyls which generate free radicals in solution.

Preliminary Mechanism

Most of the work on metal carbonyls as free radical sources was carried out by C. H. Bamford and his co-workers. In 1962, they discovered that metal carbonyls in the presence of small amounts of an organic halogen compound, such as CCl_4 , initiated the thermal polymerization of methyl methacrylate.^{2,3,4} By dilatometric techniques, the rate of polymerization for methyl methacrylate was studied as a function of metal carbonyl concentration, carbon tetrachloride concentration, and partial pressure of CO. The results obtained from these studies indicated that the process was a free radical one. Moreover, the dependencies of the rate of polymerization on $[\text{CCl}_4]$, $[\text{CO}]$ and $[\text{C}]$, where C is the metal carbonyl, suggested the following mechanism:



M is the "monomer," methyl methacrylate,
 Me is the metal (Mo, Cr, W, etc.),
 II and III are reactive intermediates, and
 R[•] is the primary radical formed.

Simple kinetic considerations for the initiation step (formation of R[•]) give:

$$V_1 = \frac{K_1 K_3 [\text{C}][\text{CCl}_4][\text{M}]}{K_2 [\text{CO}] + K_3 [\text{CCl}_4]}$$

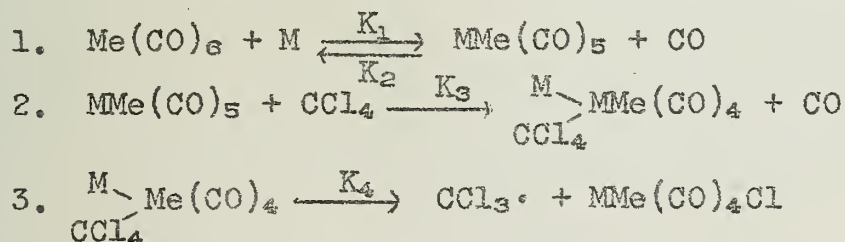
where V_1 is defined as the rate of initiation. The rate of polymerization is expressed as

$$\frac{-d[\text{M}]}{dt} = \frac{k_p}{\sqrt{k_t}} [\text{M}] V_1^{1/2}$$

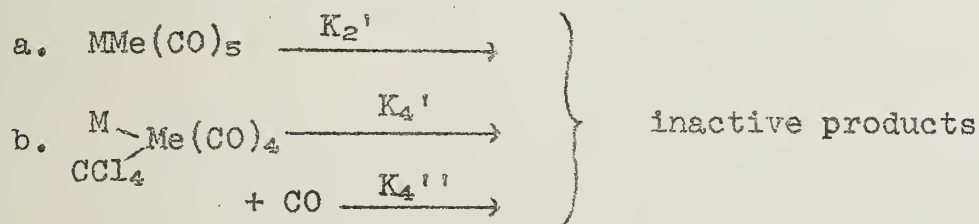
where k_p and k_t are the rate constants for the propagation and termination steps, respectively.

Detailed Mechanism

When $\text{Mo}(\text{CO})_6$ was used as the initiator, ESR studies more or less confirmed the presence of Mo^{I} species.^{5,6,7} This suggested that intermediate III is the result of an oxidation-reduction reaction forming a Mo^{I} compound and $\text{CCl}_3\cdot$ as the primary radical. A more detailed investigation on the effect of different organic halogen compounds was carried out.^{8,9} Similar studies using a polyfunctional halide, such as poly(vinyl trichloroacetate), and $^{14}\text{CCl}_4$ confirmed that the primary radical formed was $\text{CCl}_3\cdot$.¹⁰ Quantitative measurements of CO evolution were carried out and it was found that when one had only metal carbonyl in monomer solution one molecule of CO evolved per molecule of metal carbonyl, but when CCl_4 was also present, two molecules of CO evolved. This is in accord with the predicted mechanism. By extending the study to a whole series of metal carbonyls and their derivatives, Bamford and co-workers arrived at the following mechanism:^{11,21}



They also noted three side reactions:



The functional form of the rate of polymerization based on this mechanism successfully accounted for all experimental observations. A qualitative back-bonding argument was advanced by Bamford to account for the enhanced reactivity of some substituted metal carbonyls. A similar mechanism was proposed for transition metal complexes containing other multi-dentate ligands.^{22,23}

Further polymerization studies have been carried out employing an inert diluent such that the rate of polymerization could be studied as a function of the monomer concentration.^{5,24,25} For a series of metal carbonyls which are believed to undergo substitution reactions by a Sn-1 mechanism,²⁶ the above study showed a monomer order of 1.5, which according to polymerization kinetics implies a Sn-2 displacement!! A similar discrepancy was found for $\text{Mn}_2(\text{CO})_{10}$. Bamford and co-workers found that the reaction follows an Sn-1

mechanism with the initial step being:



Again this is in discord with published results.²⁸

Further Studies

A very fascinating property of the polymerization initiated by these metal carbonyl systems is the high degree of isotactic material formed. In fact, up to 30% isotactic enhancement was obtained when $\text{Ni}(\text{CO})_4$ was used. The mere fact that the presence of a metal carbonyl increases the stereospecificity of the polymer warrants further study. This stereospecificity could be applied to network formation when a polyfunctional halide is used, such as poly(vinyltrichloroacetate). This would, hopefully, give a stereospecific cross-linked polymer which could have useful applications in the field of catalysis.

Photopolymerization of methyl methacrylate was also initiated by the same metal carbonyls; with $\text{Mn}_2(\text{CO})_{10}$ being the most reactive.^{27,33} With $\text{Re}_2(\text{CO})_{10}$ as the initiator, an after-effect was observed. That is to say, even after the UV radiation was turned off, polymerization still proceeded. This after-effect was attributed to the heterolytic cleavage of the Re-Re bond during photolysis. This would form $\text{Re}(\text{CO})_4$ and $\text{Re}(\text{CO})_6$. The slow decay of electronically excited $\text{Re}(\text{CO})_6$ to the ground state was attributed to giving rise to the after-effect.

A possible use of the photoinitiation process in photography will be briefly discussed.

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STEREOCHEMISTRY OF ORGANOALUMINUM COMPOUNDS AND ION-PAIRS

(Thesis Report)

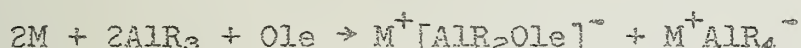
David J. Brauer

January 12, 1971

Introduction

Due to the usefulness of organoaluminum compounds as reducing agents in a wide variety of chemical reactions and as catalysts in the polymerization of olefins, organoaluminum chemistry has shown a rapid development particularly in the last ten years.¹ The dimeric structure of trimethylaluminum has posed problems for valence bond theory as applied to methyl bridged compounds and has prompted research into the stereochemistry of other polynuclear organoaluminum compounds.^{2,3} In the first part of this seminar, the relative importance of steric repulsions and electronic effects upon the stereochemistry of polynuclear organoaluminum compounds will be discussed, especially as they are related to the solid state structure of $[(CH_3)_2AlSCH_3]_n$.

Recently the syntheses of a number of organoaluminum compounds have been reported by Lehmkuhl to take place according to the following reaction:⁴



where M = Li, Na, K; R = CH₃, C₂H₅; Ole = olefin. In the second part of this seminar the results of structural investigations of the aluminate compounds, with Ole = naphthalene and anthracene, will be presented.

Results

(1) Dimethyl-μ-methanethiolaluminum(III), $[(CH_3)_2AlSCH_3]_n$

An x-ray crystal structure investigation has established that $[(CH_3)_2AlSCH_3]_n$ is an infinite polymer in the solid state. No previous polynuclear organoaluminum compound has been shown to have such a stereochemistry in the solid state. Further, the above structure is contrary to the dimeric structure predicted from gas-phase molar weight data. The stereochemistry will be discussed with respect to the valence electron distribution and the electron donor ability of the sulfur atom.

(2) Tetra(1,4-epoxybutane)disodium(I) Tetramethylbis-1,4-dihydro-1,4-naphthylenedialuminate(III), $[Na(THF)_2]_2[Al(CH_3)_2C_{10}H_8]_2$

A yellow crystalline product was isolated from the reaction of two moles of Na, two moles of Al(CH₃)₃, and one mole of C₁₀H₈ in tetrahydrofuran (THF). The crystal structure was determined by x-ray methods. The compound exists as a centrosymmetric, contact ion-pair

complex with two $\text{Na}(\text{THF})_2^+$ cations complexed to the dimeric dianion. Two 1,4-dihydro-1,4-naphthylene groups are fused into the dianion via the two dimethylaluminate species. The aluminum-naphthylenic carbon bond distances of 2.056(10) and 2.074(10) Å are significantly longer than the aluminum-methyl carbon bond distances of 1.982(11) and 1.990(12) Å. The long Al-C bond lengths are interpreted in terms of electron-deficient Al-C bonding due to the partial delocalization of the formal negative charge on the aluminum atoms onto the carbon atoms of the naphthylenic rings.

- (3) Tetra(1,4-epoxybutane)disodium(I)
Tetramethylbis-1,4-dihydro-1,4-anthrylenedialuminate,
 $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{14}\text{H}_8\text{O}]_2$

A light yellow powder was isolated from a reaction in diethyl ether of two moles of Na, two moles of $\text{Al}(\text{CH}_3)_3$, and one mole of anthracene. Recrystallization of the product from THF yielded yellow crystals, and their structure was determined by x-ray crystallographic techniques. This compound also exists as a centrosymmetric, contact ion-pair complex with two $\text{Na}(\text{THF})_2^+$ counterions complexed to the dimeric dianion. In this case, two 9,10-dihydro-9,10-anthrylenic groups are fused into the dianion by the two dimethylaluminate species. Both sets of Al-C bond lengths are equal to the corresponding sets found in $[\text{Na}(\text{THF})_2]_2[\text{Al}(\text{CH}_3)_2\text{C}_{10}\text{H}_8]_2$. The differences in the stereochemistry of the sodium ions in the last two structures will be discussed with emphasis on the role of steric repulsions in ion-pair bonding.

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HIGH-PRESSURE INFRARED SPECTROSCOPIC STUDIES OF HYDROGEN BONDING

Alan J. Pribula

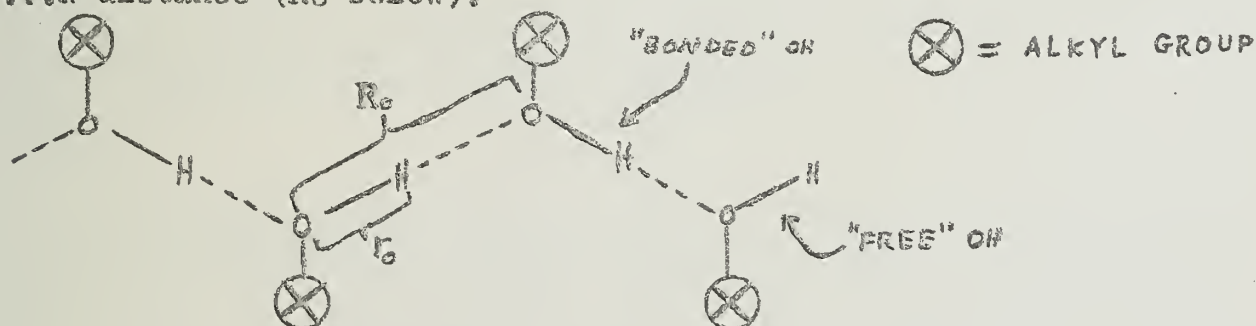
February 23, 1971

Introduction

Until recently, high-pressure spectroscopic studies have been hampered due to a lack of appropriate apparatus for the simultaneous production of the pressure and spectroscopic observation on the material under study. Drickamer and coworkers have developed apparatus for this purpose,¹ using NaCl or sapphire windows. A much simpler apparatus, using diamond as both the pressure transmission fluid and window material, was developed by Lippincott and his coworkers,² and it is this apparatus which has been used for most of the studies on hydrogen-bonded materials which will be described in this seminar. Applications of this cell to areas other than the hydrogen-bonding field are numerous, but beyond the scope of this seminar.³

Studies on Solids

The earliest studies on hydrogen-bonded solids led to the result that the frequency of ν_{OH} or ν_{NH} is decreased upon application of the high (~ 10 -100 kbar) pressure.⁴ This is interpreted as meaning a stronger hydrogen bond, due to the decreased O...O or O...N distance (R_0 below).



The quantitative results are fit by the theory of Lippincott and Schroeder⁵ relating R_0 , r_0 , and ν_{OH} . Later studies⁶ on two different crystal forms of phenol show a relationship between ν_{OH} and $\nu_{O...O}$ (essentially a lattice vibration) which supports this theory even more graphically.

Studies on single crystals⁷ grown by the application of pressure are quite enlightening for the theory of hydrogen bonding. Using polarized light, a doublet is seen for the OH stretch in n-decanol (and other alcohols), the two components of which have different bandwidths, pressure-induced frequency shifts, and polarization behavior. Isotopic dilution studies indicate that this doubling is due to coupling of vibrations, rather than to the effect of site symmetry in the solid. The decoupled (but still strongly hydrogen-bonded) OH vibration is much narrower than that usually seen for systems of this type, indicating that the intrinsic bandwidth of ν_{OH} is not much more than that for any other infrared band. The broadness is due to coupling, not to a broad potential well, or the other reasons which have been advanced.

Studies on Solutions and Pure Liquids

The earliest high-pressure infrared work on hydrogen bonding systems was performed in 1955.² Fishman and Drickamer found that the $\Delta\nu_{\text{OH}}$ ($= \nu_{\text{OH}}(\text{low pressure}) - \nu_{\text{OH}}(\text{high pressure})$) of n-butanol in various solvents varied linearly with the relative density of the solvent, squared, i.e., as $(\rho/\rho_0)^2$, where ρ = density of solvent at high pressure, and ρ_0 = density of solvent at zero applied pressure. This indicates a $1/R^6$ dependence of the energy of interaction of the alcohol with the solvent.

In studies on pure liquids,^{7a} it has been shown that very different behavior is observed on isotopic dilution than with solids, indicating that coupling is not an important factor in the bandwidths of liquid systems.

The effect of raising the pressure has also been shown to be different from that of lowering the temperature.⁹ Lowering the temperature increases the length of the alcohol chains, while increasing the pressure seems to shorten them, at least in some cases, due to steric interactions. The shorter, i.e., less associated, chains can more easily pack together and decrease the volume of the sample, as necessitated by the higher pressure. The non-hydrogen-bonded OH stretch is seen to increase in intensity upon application of higher pressure, lending support to this hypothesis. The data also indicate that this "free" ν_{OH} is due to the end of an extended chain, rather than to a monomeric molecule.

Summary

The data obtained by this technique seem to indicate that the theory of the hydrogen bond is not yet as complete as some might think, and that a new direction may be needed in the theoretical developments. A united theory, applicable to all physical states, is seen to be inappropriate, and the way has been opened for a new understanding of this important phenomenon. Comparison of the high-pressure data to that obtained at low temperature also increases our knowledge in the area.

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NMR STUDIES OF QUADRUPOLEAR NUCLEI

Robert A. La Rossa

March 16, 1971

Introduction:

The use of the proton magnetic resonance experiment as a tool for the study of chemical systems is well established. More specifically, the study of relaxation processes yields information regarding various aspects of molecular structure and motions. Relaxation effects present in the nmr of quadrupolar nuclei may in certain cases be used as sensitive probes of molecular properties. It is the purpose of this seminar to discuss some applications of relaxation studies of quadrupolar nuclei. Although a significant amount of work has been done with solids, this seminar will deal only with solution studies.

Theory:

When transitions are induced in the magnetic resonance experiment, the equilibrium distribution of the spins is disturbed, and relaxation processes are required to reestablish the equilibrium. Longitudinal and transverse relaxation, with characteristic times T_1 and T_2 which are usually equal in solution, are caused by fluctuating magnetic or, in the case of quadrupolar nuclei, electric fields.

A nucleus having spin $I > 1$ possesses a quadrupole moment which reflects the distortion of the nuclear charge from spherical symmetry. In the presence of an electric field gradient, different orientations of the nucleus have different energies. In solution, where molecules tumble, the field gradient follows the molecular motions, and the fluctuating field produced causes rapid relaxation. When present, this effect is generally the dominant relaxation mechanism. Abragam¹ presents the general equation for quadrupolar relaxation:

$$1/T_1 = \frac{3}{40} \frac{(2I+3)}{I^2(2I-1)} (1+\eta^2/3) \left(\frac{e^2 q Q}{h} \right)^2 \tau_c$$

where η is the asymmetry parameter for the electric field gradient, I is the nuclear spin, eq is the major component of the field gradient, Q is the quadrupole moment, and τ_c is the reorientational correlation time, generally considered to be the rotational correlation time. This is essentially the time required for the molecule to rotate through one radian. The quantity $e^2 q Q/h$ is the quadrupole coupling constant.

The simplest and most frequently used model for the correlation time is based on rotational Brownian motion. A sphere of radius a is considered to be rotating in a fluid of viscosity σ . It can be shown that $\tau_c = (4\pi\sigma a^3)/3kT$. A study of relaxation should provide information about the quadrupole coupling constant, and therefore structure and bonding, and about molecular reorientations in solution.

Applications:

Recent work² on ${}^7\text{Li}$ ($I=3/2$) relaxation in organolithium species of known aggregation serves to illustrate some of the basic ideas presented above. The small relaxation rates observed for the tetrameric species correlate well with the structure which had been proposed previously for these aggregates. Unusual relaxation times for $(\text{CH}_3)_3\text{Si}(\text{CH}_2)\text{Li}$ and CH_3Li are explained in terms of structural changes.

In 1966, Stengle and Baldeschwieler suggested a method for studying macromolecules in NaCl solutions using ${}^{35}\text{Cl}$ ($I=3/2$) nmr,³ and a number of studies using this technique have been reported.⁴⁻⁸ The ${}^{35}\text{Cl}$ linewidth is broadened due to interaction of Cl^- ions with natural sites, such as metal sites in metalloenzymes, or with labels such as Hg bonded to the macromolecule. The linewidth, in the limit of rapid exchange between free and bound chloride, reflects the availability of binding sites, the Cl -metal bonding interactions, and motional restriction at the binding sites under variable conditions.

Happe and Ward^{9,10} applied the halide technique to a study of complex formation of Zn^{2+} with nucleotide diphosphate ligands. The contribution of various species to the ${}^{35}\text{Cl}$ linewidth were determined using known equilibrium constants for protonation of the ligands. For the $\text{Zn}(\text{ADP})^-$ system (ADP = adenosine diphosphate) as well as for $\text{Zn}(\text{CDP})^-$ (CDP = cytidine diphosphate), enhanced relaxation was attributed to an increase in τ_c for the complexes due to internal chelation with the nucleotide base.

Similar techniques have been applied using ${}^{43}\text{Ca}$ ($I=7/2$)¹¹ and ${}^{23}\text{Na}$ ($I=3/2$).^{12,13} The ${}^{23}\text{Na}^+$ ion has been used to study complex formation with amino-polycarboxylates, and it was found that bonding to nitrogen is important in the complexes.

The hydrolysis of $\text{Al}(\text{H}_2\text{O})_6^{+3}$ has been studied by ${}^{27}\text{Al}$ nmr.¹⁴ There has been some question whether $\text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}$ is monomeric or polymeric. The estimated linewidth for $\text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}$ along with linewidth data available for alkyl aluminum dimers¹⁵⁻¹⁷ and $\text{Al}(\text{H}_2\text{O})_5(\text{HSO}_4)^{+2}$ prompted the suggestion that the broadening found for $\text{Al}(\text{H}_2\text{O})_5\text{OH}^{+2}$ is due to association.

Conclusion:

The relaxation times for quadrupolar nuclei provide a sensitive indication of quadrupole coupling constants and rotational correlation times. Unfortunately, the lack of simple methods for determining accurate rotational correlation times makes it difficult to quantitatively evaluate changes in quadrupolar interactions. Some modifications to the Debye rotational Brownian motion model have been attempted with some success,^{18,19} and suggestions have been made regarding correlation times in macromolecules.^{20,21} Nevertheless, relative differences in quadrupole coupling constants and

rotational correlation times can be used in conjunction with other chemical evidence to solve interesting chemical problems.

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CARBON-BONDED BETA-DIKETONE COMPLEXES

Thomas E. Boyd

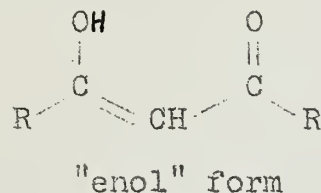
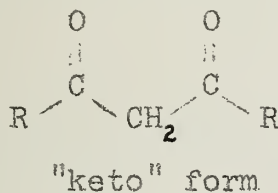
March 30, 1971

Introduction

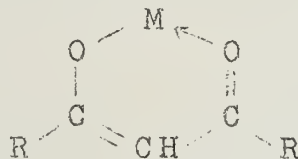
Beta-diketone complexes are known for virtually every metal, along with some of the non-metals and metalloids as well. Complexes in which the ligand is chelated to the metal atom by way of the oxygen atoms have been known and recognized for a very long time, but it was only recently discovered that such ligands can also bond to metals through the beta carbon atom. Compounds containing such metal-carbon bonds were reported by Werner as early as 1901,¹ but the true nature of their bonding has come to light only recently. The purpose of this seminar will be to compare and characterize the carbon-bonded complexes with respect to the oxygen-bonded ones and to discuss examples of known complexes, illustrating the variety of compounds to which this type of bonding gives rise.

Characteristics of the Complexes

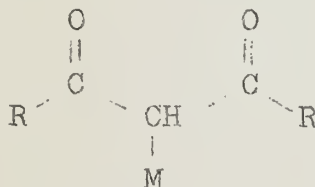
Beta-diketones can assume two tautomeric forms in the pure state or in solution:



Of these, the enol form tends to predominate, and is the form which chelates with the metal atom in oxygen-bonded complexes as shown below:



In the carbon-bonded species, on the other hand, the ligand is in the keto form:



Infrared spectroscopy is most useful in differentiating between the two types of complex. In the oxygen-bonded complexes the carbonyl stretching frequencies are about 100 cm^{-1} lower than in carbon-bonded complexes. For the latter, the methylene carbon-hydrogen out-of-plane bending frequency is absent and metal-carbon stretching frequencies are observed ($500\text{-}600\text{ cm}^{-1}$) instead of those for metal-carbon stretching ($350\text{-}500\text{ cm}^{-1}$).²

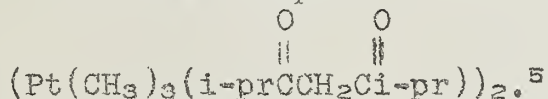
Nuclear magnetic resonance is not as useful unless there is spin-spin coupling with the metal atom. When such is the case, the resonance for the methylene proton will be split considerably in the carbon-bonded complex and hardly at all in an oxygen-bonded one.

Carbon Bonding

Nyholm states that metal-carbon bond strength increases in going down the periodic table. It also increases with the π -bonding capacity of other ligands on the metal and with the electronegativity of substituent groups on the bonding carbon atom.³ The carbon-bonded beta-diketone complexes are formed almost exclusively with the heavier third row transition metals. Their electronegativity is higher than would be predicted otherwise. Just as more electronegative species, such as halogens, bond to a carbon atom in preference to oxygen, so it is among these heavier metals, as observed in their capacity to form metal-carbon bonds.

Compounds

The first carbon bonded beta-diketone complex to be prepared was $\text{KPt}(\text{acac})_2\text{Cl}$, but the nature of its bonding was not recognized until much later.⁴ The first complex found to contain such a carbon-bonded ligand was



variety of compounds of platinum as well as iridium, gold, and mercury have been reported and characterized.⁶⁻¹¹ Since this time, a

Conclusion

This area of chemistry will be a very fertile field for further study. Platinum has displayed a rather rich chemistry in this area, and it would be reasonable to expect similar behavior of some of the other metals cited earlier. However, the field seems to be somewhat dormant at the present time as very little has been published since Gibson's review² went to press.

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Spectroscopic and Diffraction Studies of the Aquated Proton
in the Solid State

Arlene R. Mootz

April 20, 1971

As early as 1924, Volmer postulated the existence of the oxonium ion, H_3O^+ , on the basis of the similarity of the X-ray powder patterns of NH_4ClO_4 and $\text{HClO}_4 \cdot \text{H}_2\text{O}$.¹ Later investigations,²⁻¹³ using spectroscopic (IR, Raman, nmr) and diffraction (X-ray and neutron) techniques found the structure of the oxonium ion to be analogous (but flatter) to that of crystalline ammonia. The ion was found to be present in the crystalline monohydrates of the strong acids: HNO_3 , H_2SO_4 , HX ($\text{X} = \text{halide}$), HClO_4 .

Higher hydrates of the aquated proton $\text{H}^+(\text{H}_2\text{O})_n$ have also been investigated. The major (nearly all) part of these studies involved X-ray and neutron diffraction.¹⁴⁻²⁴ Experimental data seems to indicate that the H_3O^+ and H_5O_2^+ ions are distinct species in the crystalline state, the latter being formulated as $(\text{H}_2\text{O}-\text{H}-\text{OH}_2)^+$, not $\text{H}_3\text{O}^+(\text{H}_2\text{O})$. The H_4O_2^+ ion exhibits three conformations in the solid state: cis (boat form), trans (chair form), and gauche. These conformations are determined by the strength of the hydrogen bonds formed and the effects of crystal packing.

The studies of the nature of these aquated proton species are still incomplete. There have been no neutron diffraction studies of the oxonium salts and further elucidation of the H_5O_2^+ species also awaits additional neutron diffraction studies. The suggestion of a double minimum function in the neutron study of $\text{HAuCl}_4 \cdot 4\text{H}_2\text{O}$ poses interesting questions.¹⁶

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PHOTOCHEMICAL SUBSTITUTION OF METAL CARBONYL COMPLEXES

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April 27, 1971

Introduction

Photochemical reactions of metal carbonyl systems have been known since 1905 with the photochemical production of $\text{Fe}_2(\text{CO})_9$ from $\text{Fe}(\text{CO})_5$ in sunlight.¹ Since then, photochemistry has been used mostly by the organic chemist. With metal carbonyl complexes, the photochemical reaction is usually a substitution reaction where a Lewis base present in the reaction mixture replaces a carbonyl. This approach has been used for years to prepare simple substituted metal carbonyls not possible through thermal reactions. Recently, workers have extended the synthetic techniques associated with photochemical reactions to the point where the inorganic chemist should consider the photochemical synthetic route as practical as the thermal route.

Photochemical Background

Because of the popularity of photochemistry in organic chemistry, much work has been done to explain what happens when a molecule absorbs a photon of visible or ultraviolet radiation, leading to a photochemical reaction. Either directly or through a series of energy transfers the excited molecule reaches a long-lived excited state. At this point, either a photophysical deactivation such as fluorescence or phosphorescence is possible, or the excited molecule may undergo a chemical reaction. This seminar is concerned with these photochemical deactivations of electronically excited metal carbonyls.

With metal carbonyl systems, this photochemical excitation leads to the direct dissociation of a carbonyl. Some authors feel that this dissociation is the result of a transfer of an electron from an orbital localized at the metal to one localized at the ligand. Such a concept is referred to as a charge transfer from the metal to the ligand (CTML).² Another possibility is that the metal ligand bond develops enough antibonding character in its excited state that a rupture of the bond follows. Regardless of the mechanism, the coordinately unsaturated species have been identified in glasses and inert gas matrices at very low temperatures, supporting the concept of a dissociative mechanism.^{3,4,5,6} More work is needed in this area to fully understand the nature of these intermediates. The final step in the photochemical reaction is the combination of this unsaturated intermediate with another good electron donor.

The beauty of photochemical substitution of metal carbonyls lies in the fact that the mechanism always involves a complete dissociation before product formation at any temperature. This results in simple first order kinetics,⁷ whereas it has been shown that the same systems under thermal substitution follow a two term rate law.⁸

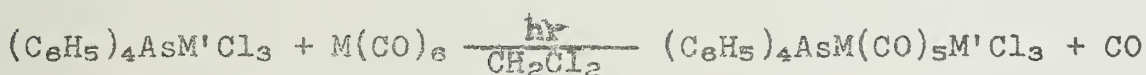
$$\text{Rate} = k_1[\text{complex}] + k_2[\text{complex}][L]$$

In this proposal, both the dissociative pathway and an associative route are employed. Similar to the organic S_N2 reaction mechanism, the carbonyl group is leaving and bond breaking as the new ligand is entering and bond making. The end result is that the photochemical route can be employed at any temperature, whereas the thermal route is dependent on a higher temperature for activation. Also, the thermal pathway varies in mechanism as the substituents on the metal carbonyl change, but the photochemical route always follows a completely dissociative mechanism.⁹

Photochemically Substituted Metal Carbonyls

The number of carbonyls produced by photochemical substitution is convincing proof of the versatility of the technique. For the common Lewis bases, the list of possible products is enormous and most have been photochemically synthesized. Good reviews have appeared which extensively list these products, and it is apparent that, for the common bases, any number of the carbonyls can be replaced.^{10,11,12}

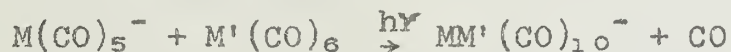
Recent interest has been with the use of novel "Lewis bases" to photochemically produce products M(CO)_{n-m}B_m where B is an olefin or another metal.¹³ In the reaction



where M = Cr, Mo, and W M' = Sn or Ge,

a metal-metal bond results with the M'Cl₃⁻ species acting as the electron donor substituent. The similar thermal preparations of many of these complexes have been reported, but with limitations to cobalt-tin and cobalt-germanium bonds.¹⁴

Reactions of the type¹⁵



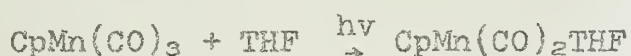
where M = M' = Cr, Mo, and W, have resulted in mixed metal-metal bonds between transition metals. Through this procedure thermally unobtainable metal-metal anions such as FeMn(CO)₉⁻ and FeCo(CO)₈ have been prepared. Similar reactions for halogen substituted metal carbonyls result in dinuclear anions with bridging halogen

groups.^{16,17}



M is Cr, Mo and W.

Another active area of this research has been where an olefin is used as an electron donor for substitution. From the mixed metal carbonyl, cyclopentadienyl manganese tricarbonyl, a series of complexes of the type $CpMn(CO)_2$ (olefin) have been prepared through an indirect photochemical procedure.¹⁸ In this technique, a coordinating solvent such as THF is used to stabilize the unsaturated intermediate until the olefin enters.^{19,20}



Along this same line, other "half sandwich" complexes such as hexaalkylborazole chromium tricarbonyl derivatives can be photochemically prepared directly from the metal carbonyl and the borazole. In these cases, the complexes are thermally inaccessible from the metal carbonyl since the free ligands will decompose at the temperatures required for the thermal synthesis.²¹

Conclusion

Whenever a substituted metal carbonyl complex is sought which might be thermally unstable or would require an intolerable temperature to prepare, the photochemical pathway should be considered. Even when a thermal technique is known, the photochemical pathway should be considered with the possibility of a better yield or a more direct route. Unfortunately, photochemistry has been either ignored or considered as a last resort by the synthetic inorganic chemist. Only recently has the versatility of the technique been opening the door to a brighter future.

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- LANTHANIDE NMR SHIFT REAGENTS

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April 29, 1971

Nuclear magnetic resonance spectroscopy has been used successfully for structural determination in simple molecular systems. In more complex systems, it has found only limited use because resolution of chemical shifts for magnetically similar resonant nuclei is difficult to impossible with previously existent techniques. However, satisfactory resolution has been obtained in various monofunctional organic systems through use of so-called "shift" reagents. Interaction with these reagents enhances magnetic nonequivalence in the resonant nuclei and "shifts" the normally overlapping resonances asunder. In addition, the spectra obtained frequently show simple first order splitting.

The shifts are affected by either a contact (through bond) or a dipolar (through space) mechanism.¹⁻⁴ The contact shift mechanism requires a delocalization of electron density between the shift reagent and the molecular system.⁹⁻¹¹ The dipolar shift, sometimes called the pseudocontact shift, requires the presence of a magnetic moment in the shift reagent.⁵⁻⁸ The reagents intensively studied recently are some tris- β -diketone chelate complexes of lanthanides.

Lanthanide(III) ions have unpaired electrons that occupy 4f orbitals beneath filled 5s and 5p orbitals and are therefore unavailable for bonding or significant delocalization onto ligands. These ions thus are limited to dipolar magnetic interactions. They also possess a rather short electronic relaxation time which is a requirement for the observation of relatively sharp resonances. Of the lanthanide ions, Pr(III) and Eu(III) are found to give optimum ratios of line-broadening to line-shift.¹⁸

Tris-(2,2,6,6-tetramethylheptane-3,5-dionato)europium(III), [Eu(thd)₃], has been the most extensively used lanthanide shift reagent. This compound is also known by the trivial name of tris-(dipivalomethanato)europium(III), [Eu(DPM)₃]. It readily increases coordination number in solution to accommodate a wide variety of Lewis bases in a rapid, reversible Lewis acid-base interaction.²¹⁻²⁵ The order of this interaction with some functional groups is as follows:



The ground state of Eu(III) is ⁷F₀ and diamagnetic as a result of strong Russell-Saunders spin-orbit coupling. There are, however, two thermally accessible excited states, ⁷F₁ and ⁷F₂, which contribute appreciably to the magnetic moment. The distribution over these three states is estimated to be 1.0:0.59:0.09 at 25°. ²⁰ Eu(III) complexes exhibit temperature dependent paramagnetism through first and second order contributions from excited states.

Dipolar shifts have been quantitatively characterized in theory² developed for a point dipole having only one thermally populated energy level (in the absence of a magnetic field) whose states can be assigned a spin quantum number S and, for $S \geq 1$, whose zero-field splittings can be ignored. Further, any orbital contribution to the isotropic nmr shift is taken into account through use of g -tensor components. This last assumption requires that there be at most only a first order orbital contribution to the magnetic moment of the complex, brought on by spin-orbit mixing of the ground level with nonpopulated excited states. Clearly, this model does not coincide exactly with the Eu(II) ion. Some efforts have been made to rectify discrepancies by accounting for possible first order contributions from thermally excited states, but these efforts have not yet yielded satisfactory results.⁶⁻⁸

However, some generalities can be made using this model despite its limited applicability. The shift can be taken to be the product of three functions:

$$H/H_0 = G(\theta, \varphi, g) * F(J, T) * (1/r^3)$$

where r is the distance between the metal atom and the resonant nucleus; θ and φ are angles that describe the orientation of the resonant nucleus with respect to the principle magnetic axis; and the other symbols have their usual meaning. The shift could be calculated from a knowledge of g -tensor values and the geometry of the molecule. Usually, only the radial geometry is known with any certainty in the form of an average distance of closest approach calculated under the assumption that the coordinated molecule freely rotates about the line of centers between the metal atom and the site of coordination. Plots of observed shifts versus radial function usually lead to approximately straight lines as expected for a predominate dipolar mechanism. But shifts for resonant nuclei closest to the metal atom, that is, within three or four bonds, fall far off the lines. This discrepancy has been attributed to significant contact (through bond) interactions, but convincing supporting evidence has been reported in only one case.²⁹

The chemical literature contains many reports on the application of lanthanide shift reagents as a tool in the elucidation of spectra from relatively complicated organic systems.¹²⁻¹⁷ These range from a simple demonstration of reagent efficacy to actual use in determination of unknown structures. Some particularly interesting applications also have been reported in the area of biochemical systems.³¹⁻³⁴ The role of metal ions in these systems is being investigated through elucidation of coordination sites in addition to just structural determinations. Other reports deal with improvement and understanding of the technique.^{17,27-29}

An Annotated reference list follows that will indicate where more detailed sophisticated information about lanthanide shift reagents can be found.

For general information on theory of chemical shifts effected by paramagnetic species, the following are a must:

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THE NUCLEAR OVERHAUSER EFFECT

Cheryl A. Deckert

May 4, 1971

Introduction

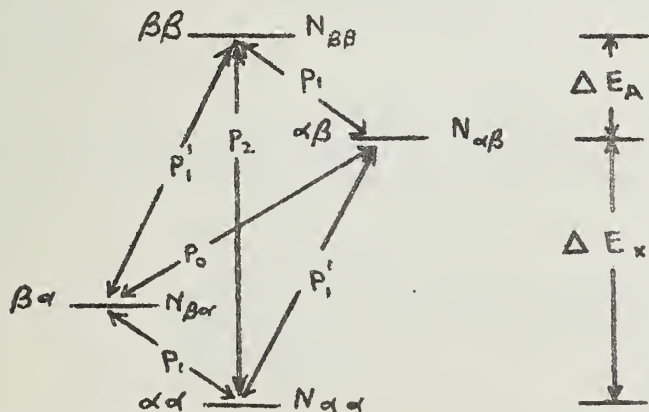
The Nuclear Overhauser Effect (NOE) is a phenomenon sometimes observed in nuclear-nuclear double magnetic resonance experiments.¹⁸⁻²² NOE should be differentiated from the original Overhauser effect² (OHE), which arises from electron-nuclear interaction. In both cases, one spin in the system is saturated (a nuclear spin in NOE; an electronic spin in OHE) while nuclear transitions are simultaneously induced and observed at low field strength. Under proper conditions, the result is a change in intensity (usually positive) of the nuclear signals over those seen in the absence of saturation. In OHE, the intensity increase may be several-hundredfold; it is used mainly for detection of weak signals (e.g., C^{13} or P^{31}). In NOE, the enhancement is much less dramatic (less than 50% for proton-proton interaction), but because of the origin of the effect, it can be readily used for structural determination or spectral assignments.

Although Bloch³ extended Overhauser's original theory to the nuclear-nuclear case in 1954, NOE did not come into use as a chemical tool until Anet and Bourn's work in 1965.⁸ Up till now, only organic systems have been studied, but the application to inorganic molecules (particularly organometallics) seems likely.

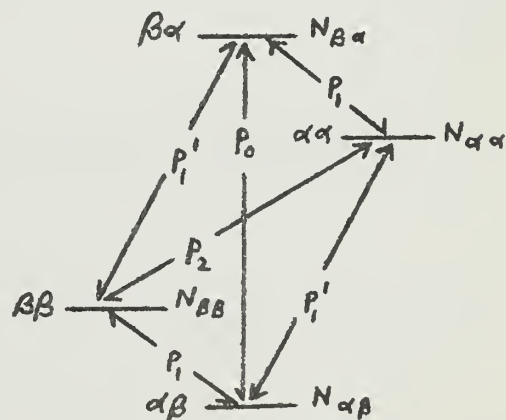
Theory¹⁻⁵

If the dipole-dipole (d-d) mechanism is the main process affecting the spin-lattice relaxation process at the observed nucleus, then saturation of the other (nonequivalent) nucleus can lead to enhancement of the absorption signal.⁴ Since the intramolecular d-d interaction of the two nuclei is proportional to the inverse sixth power of their internuclear distance,^{4,5} only those nuclei at short distances from each other can exhibit NOE.

Consider the energy level diagram for the AX system,¹⁸ both having spin 1/2. Spin-spin coupling is neglected.



A. Both gyromagnetic ratios are positive.



B. The gyromagnetic ratios are of opposite sign.

We are interested in the intensity of the A transition signals. The intensity of A is proportional to the population difference $N_{\beta\beta} - N_{\alpha\beta}$ or $N_{\beta\alpha} - N_{\alpha\alpha}$.¹ At thermal equilibrium, the population distribution is given by the Boltzmann factor $N_{\text{upper}}/N_{\text{lower}} = \exp(-\Delta E_a/2kT)$.¹

If nucleus X is saturated, however, levels connected by X spin transitions become equally populated, i.e., $N_{\beta\beta} = N_{\beta\alpha}$ and $N_{\alpha\beta}$ and $N_{\alpha\alpha}$.

It has been shown that for a d-d relaxation mechanism, transition probability p_2 predominates.^{4,18} Thus, transitions between states $\beta\beta$ and $\alpha\alpha$ occur rapidly compared with the other relaxation processes. Since the X upper spin levels are constantly being repopulated, the result is a pumping action which continuously increases the population differences between the A spin levels in the case where the gyromagnetic ratios are both positive, and decreases these differences where the gyromagnetic ratios are of opposite sign. The signal intensity changes accordingly.

Solomon⁴ has shown that under these conditions

$$\bar{A}_z = A_0 + 1/2 X_0$$

where \bar{A}_z is the observed signal intensity, A_0 the "normal" signal intensity of nucleus A at low power levels, and X_0 the "normal" intensity of X.

Since A_0 and X_0 are related by $A_0/X_0 = \gamma_a/\gamma_x$, we have

$$\bar{A}_z = A_0 (1 + 1/2 \gamma_x/\gamma_a)$$

and the enhancement factor is

$$\frac{\bar{A}_z - A_0}{A_0} = 1/2 \gamma_x/\gamma_a$$

Note that if the two nuclei have γ 's of opposite sign, and if $|\gamma_x| > 2|\gamma_a|$, a negative signal can result. No experiment of this sort has yet been reported.

Experimental

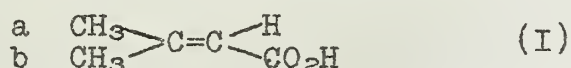
Observation of NOE depends on predominance of the intramolecular dipole-dipole interaction. This relaxation mechanism will usually predominate⁵ if certain precautions are taken:

- 1) Use a solvent containing no strongly magnetic nuclei (H^1 or F^{19})
- 2) Exclude all paramagnetic species¹⁷ (Degas sample carefully)
- 3) Limit experiment to spin 1/2 nuclei (to avoid quadrupolar relaxation).

In determining signal enhancement, care should be taken to obtain the total integrated intensity, since spin decoupling may cause the central peak of a multiplet to grow, even in the absence of an NOE.²³

Applications⁸⁻¹⁷

Anet and Bourn's work⁸ dealt with the spectral assignment of the methyl resonances in β,β -dimethyl acrylic acid (I).



Saturation of either methyl group caused collapse of the proton septet to a quartet (spin decoupling), but more significantly, irradiation of the upfield methyl resonance caused an increase of 17% in the integrated area of the proton signal. Since no such increase occurred when the other methyl signal was irradiated, the upfield resonance was assigned to methyl group a, the one closer to the proton.

In several cases, NOE's have been observed between protons which are several bonds apart, but whose molecular configuration locks the nuclei close to each other. Such observations^{8,9a} have aided greatly in structure determination.

The first case of C^{13} NOE was observed in formic acid,¹³ where an enhancement of 2.98 (same as theoretical enhancement) in the C^{13} signal occurred upon saturation of the carbon-bonded proton.

It is usually the case that the saturating field also causes spin-spin decoupling, hence loss of spectral information. Feeney, et al.,¹⁵ found that applying and then removing the decoupling field immediately before examining a spectrum allowed retention of spin-spin information, as well as some of the Overhauser intensity enhancement.

In a very interesting case, Bell and Saunders¹² observed both positive and negative NOE's in an all-proton system. The negative effects occurred between two protons separated by an intervening proton. The authors advanced a non-rigorous explanation for the effect.

Future

As mentioned above, it seems likely that the extension of NOE to inorganic systems is forthcoming. A possible application is in the conformational analysis of rigid ligands.

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MASS SPECTROSCOPY OF TRANSITION METAL CARBONYLS

Richard P. Zerger

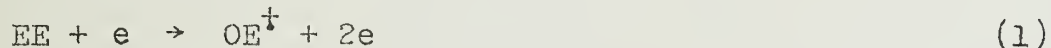
May 6, 1971

Introduction

Mass spectroscopy first began to be applied extensively to the study of transition metal organometallic compounds in 1965, although scattered papers in this area had appeared as early as 1955 including particularly Friedman, Irsa, and Wilkinson's¹ now classic study on the mass spectroscopy of biscyclopentadienylmetal derivatives. The time lag between the surge of interest in the use of this technique in organic and in inorganic chemistry does not reflect the relative importance of this field in the two divisions of chemistry, but more the difficulties of handling metal-containing compounds in conventional instruments. The basic theory² and organic aspects^{3,4} of mass spectrometry are well established and sufficient is known of the behavior of organometallic compounds^{5,6,7} in the mass spectrometer so that a comparison of the two types of compounds can be made.

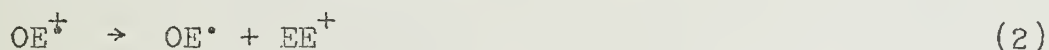
Fragmentation

The stream of vaporized sample molecules entering the ion source interacts with the beam of electrons to first form the molecular ion in the following way:

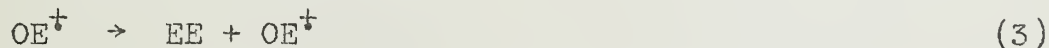


where the even-electron molecule becomes an odd-electron molecular ion. An odd-electron ion, such as the molecular ion, may decompose through one of two general pathways:

- (a) Loss of an odd-electron radical to yield an even-electron ion:

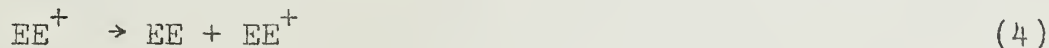


- (b) Loss of an even-electron molecule to yield an odd-electron ion:

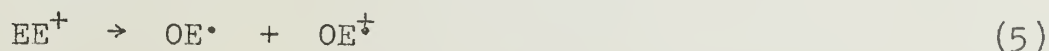


Decomposition of an even-electron ion can also proceed through two pathways:

- (c) Loss of an even-electron molecule to yield an even-electron ion:



- (d) Loss of an odd-electron radical to yield an odd-electron ion:



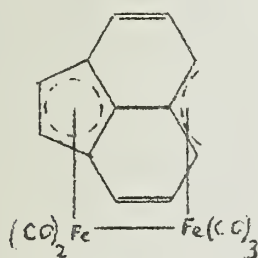
Many of the differences between electron-impact behavior of organometallic and organic compounds arise from the low M-C and M-H (M = metal) bond strengths compared with those of C-C and C-H. The greater electronegativity of carbon and hydrogen than of metals means that when a positive ion decomposes, the charge is most often retained by the metal-containing fragment. With main-group organometallics, molecular ions usually decompose by radical elimination (2). In subsequent fragmentation, process (4) is the dominant feature.

Transition-metal complexes such as carbonyls often show molecular ions of high abundance and the fragmentation behavior is not dominated by odd- and even-electron considerations. This difference may be accounted for if primary ionization involves the removal of an electron from an essentially non-bonding orbital. The ligands of organotransition metal compounds produce the main characteristics of the spectra, the influence of the metal being subtle. Mass spectra of metal carbonyls exhibit stepwise loss of carbonyl groups from the molecular ion. This metal-carbon bond cleavage is such a favored fragmentation pathway that it predominates over most other alternatives in the mass spectra of metal carbonyls containing other ligands.

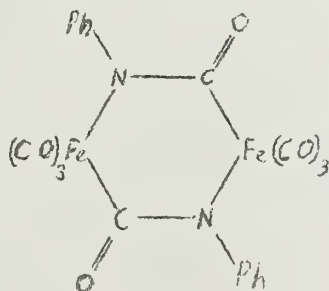
Applications

From the reaction of $\text{Fe}_3(\text{CO})_{12}$, 1,4-dibromobutylene-2 and zinc, Nakamura and co-workers⁸ obtained a complex which they formulated as the diiron pentacarbonyl, $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_5$. King^{9,10} reported that the mass spectrum of this compound exhibited the ion, $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6^+$, indicating that the correct formulation of this complex to be the diiron hexacarbonyl, $\text{C}_4\text{H}_4\text{Fe}_2(\text{CO})_6$. The diiron hexacarbonyl formulation for the analogous tetraphenylbutatriene derivative has been confirmed by X-ray crystal structure data.¹¹

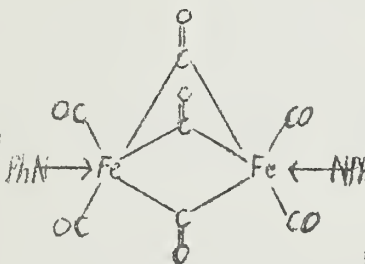
King and Stone¹² obtained a complex from the reaction of $\text{Fe}_3(\text{CO})_{12}$ and acenaphthylene which they formulated as $\text{C}_{12}\text{H}_8(\text{Fe}(\text{CO})_3)_2$. The mass spectrum reported by King⁹ shows the ion of highest mass as being $\text{C}_{12}\text{H}_8\text{Fe}_2(\text{CO})_5^+$, indicating the complex to be the diiron pentacarbonyl, $\text{C}_{12}\text{H}_8\text{Fe}(\text{CO})_5$. This formulation was later confirmed by X-ray crystallography¹³ which indicated structure (I).



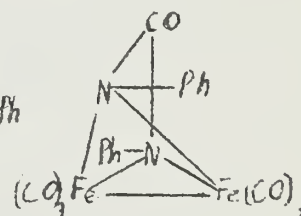
(I)



(II)



(III)



(IV)

Structure (II) was first proposed by Manuel¹⁴ for the product of $\text{Fe}_3(\text{CO})_{12}$ and phenyl isocyanate. Later, Manuel reformulated his compound, $(\text{C}_6\text{H}_5\text{N})_2\text{Fe}_2(\text{CO})_7$, and reassigned to it structure (III).¹⁵ King¹⁶ reported that, in the mass spectrum of $(\text{C}_6\text{H}_5\text{N})_2\text{Fe}_2(\text{CO})_7$, the ion, $(\text{C}_6\text{H}_5\text{N})_2\text{COFe}_2^+$, is more than twice as abundant as any other ion containing carbonyls. This suggested that the last carbonyl is lost with much greater difficulty, and King proposed structure (IV) which was later confirmed by X-ray.¹⁷

Winters and Kiser¹⁸ as well as Bidinosti and McIntyre^{19,20,21} have used mass spectrometry to determine the metal-metal bond dissociation energies of $\text{Mn}_2(\text{CO})_{10}$ and $\text{Co}_2(\text{CO})_8$. By the introduction of $\cdot\text{Mn}(\text{CO})_5$ and $\text{Mn}_2(\text{CO})_{10}$ into the mass spectrometer, the ionization potential of $\cdot\text{Mn}(\text{CO})_5$ and the appearance potential of $\text{Mn}(\text{CO})_5^+$ respectively were obtained by Bidinosti and McIntyre.¹⁹ These were then used to calculate the dissociation energy. They were also able to determine ΔH for the reaction, $\text{Mn}_2(\text{CO})_{10} \rightarrow 2 \cdot\text{Mn}(\text{CO})_5$.²¹

Mass spectrometry was used in two ways by Robinson and co-workers²² to characterize $\text{H}_2\text{Ru}_4(\text{CO})_{13}$. The mass spectrum was used for an accurate determination of the number of hydrogens present, and to determine that the hydrogens were bridging, since bridging hydrogens are more strongly retained during fragmentation.

Conclusion

From the above, it is evident that mass spectrometry is a valuable tool for the characterization of transition metal carbonyls as well as other organometallic compounds and can be used in the following ways:

1. Determination of molecular weights and composition.
2. Determination of ionization potentials and bond energies.
3. Determination of structure.

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STRUCTURAL STUDIES OF PYRIDINE DIOXIME COMPLEXES OF NI(II) AND NI(IV)

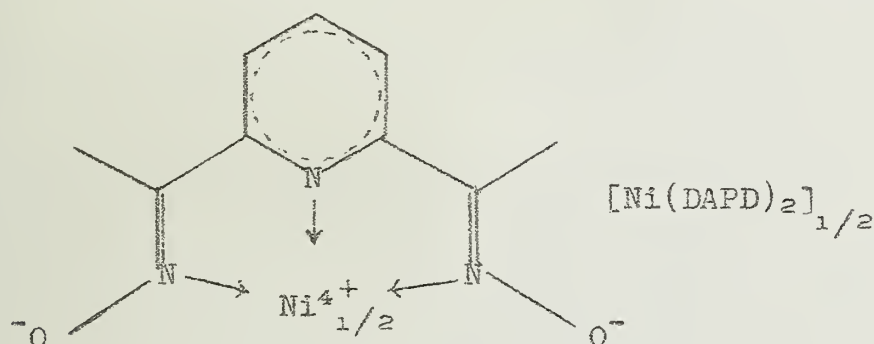
(THESIS REPORT)

Gordon D. Sproul

May 11, 1971

Introduction

Recent molecular orbital calculations and spectral data indicate that the compound bis(2,6-diacetylpyridinedioxime) nickel(IV), $[\text{Ni}(\text{DAPD})_2]$, can best be represented as a Ni(IV)



complex.¹ Such Ni(IV) complexes are comparatively rare, and no X-ray structural studies had been carried out on the Ni(IV)-oxime complexes, the most populous group of Ni(IV) compounds. It was of interest to verify by crystallographic means that this is a true Ni(IV) complex and to determine the ligand to metal bond distance.

Results

In a true Ni(IV) complex, one would expect the Ni-ligand bond distance to be significantly shorter than in an analogous Ni(II) complex. Therefore, various alkali metal salts of the Ni(II) complex $\text{Ni}(\text{DAPD})_2^{2+}$ were synthesized and one of these, $[\text{Li}(\text{MeOH})_4]_2[\text{Ni}(\text{DAPD})_2]$, was crystallized. Actually, two different crystalline habits were formed from slightly different growth media. One of these habits, which appeared to belong to a tetragonal space group, was shown by preliminary X-ray photographic techniques to be very probably a systematically twinned form of the other, orthorhombic, crystalline habit. Intensity data were collected on a crystal of the orthorhombic ($P2_12_12_1$) habit, and the structure was solved by Patterson techniques--including methods similar to the minimum function procedure.²

The Ni(IV) complex was synthesized in a manner similar to that previously reported.¹ Preliminary X-ray photographic data indicated that crystalline $\text{Ni}(\text{DAPD})_2$ belongs to the space group

$I4_1/a$; this space group requires the Ni atom to lie on a $\bar{4}_1$ center. A Fourier map based on heavy atom (Ni) phases indicated all non-hydrogen atoms. Refinement with inclusion of all atoms resulted in a structure with very small errors (conventional residual index $R = 0.025$).

Inspection of literature values for Ni(II)-N coordination distances revealed a very interesting relationship. The average coordination distance for octahedral N_6 complexes is $2.10 \pm .10 \text{ \AA}$, while that for tetrahedral N_4 complexes is $1.95 \pm .01 \text{ \AA}$ (for square-planar N_4 complexes the distance is $1.88 \pm .04 \text{ \AA}$). These average distances are not obviously related to the oxidation state of the N or to the electronic nature of the ligand. The compression factor for the metal to ligand distance in going from octahedral to tetrahedral coordination, 0.93, is very similar to the value, 0.95, calculated by Pauling³ for the compression factor for ionic crystals in which the number of nearest neighbors changes from six to four.

The Ni(II)-N bond distances found in $Ni(DAPD)_2^{2+}$ average 2.08 \AA , a value very close to that predicted for this bond. The corresponding distance in the d^6 Ni(IV) complex, averaging 1.93 \AA , is 0.15 \AA shorter than for that in the analogous Ni(II) complex. This verifies that $Ni(DAPD)_2$ is a true Ni(IV) complex. Comparison can be made with distances in Co hexamine complexes; in the d^6 Co(III) complex, the Co-N distance is 0.18 \AA shorter than in the d^7 Co(II) complex. Although electrostatic attraction contributes to the shortening of the higher oxidation state metal to ligand bond, the loss of σ^* electrons from the metal e_g orbitals is probably the greatest contributor to the bond shortening.

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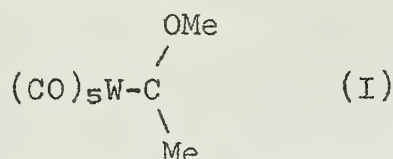
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TRANSITION METAL CARBENE COMPLEXES

Michael R. Walczak

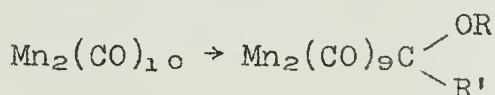
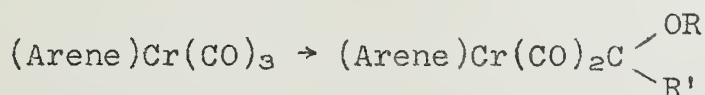
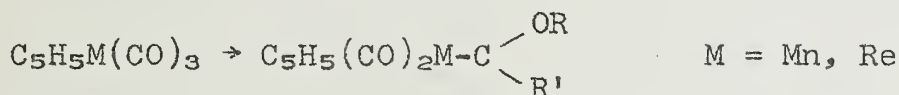
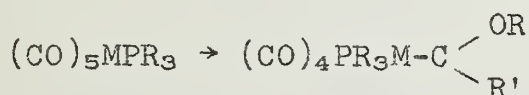
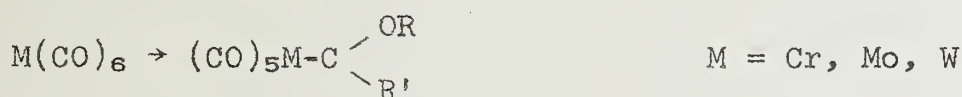
May 13, 1971

In 1964 Fischer and Maasbøl reported the preparation and characterization of a transition metal complex containing the ligand methoxycarbene.¹ The complex, (methoxycarbene)penta-carbonyltungsten (O) (I), was the first example of a transition



metal carbene complex; since then, many more compounds containing carbenes as ligands have been reported, and today, carbene complexes of Fe,²⁻⁸ Pd,⁸ Pt,⁹⁻¹³ Cr, Mo, W, Mn, and Re are known. The synthesis, structure, bonding, and applications of carbene complexes of groups VI and VII transition metals will be discussed.

Two synthetic routes have been primarily used to prepare carbene complexes. The most widely employed reaction has been treatment of a transition metal carbonyl compound with one equivalent of an organolithium reagent, followed by alkylation using aqueous acid/diazomethane¹⁴ or trialkyloxonium tetrafluoroborate¹⁵ to give the alkoxy carbene complex. All proposed intermediates in the reaction have been isolated and characterized using IR and NMR.^{14,16} Using this route, the following carbonyls have been converted to the corresponding alkoxy carbene complex:^{14,16-20}



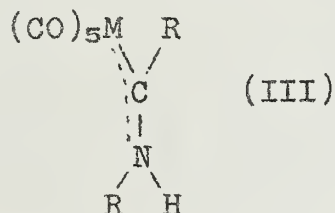
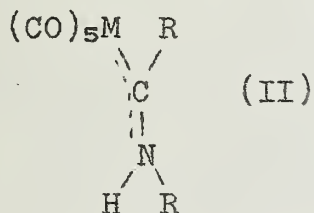
The second method of preparation involves reaction of an alkoxy carbene complex with a nucleophile, usually one containing an acidic proton, to replace oxygen with another hetero atom, either nitrogen or sulfur. Ammonia,²¹ primary amines,^{22,23} oximes,²⁴ thiophenol,²¹ and cyclohexylisocyanide^{15,25} give the following complexes, respectively: $(\text{CO})_5\text{MC}(\text{NH}_2)\text{R}$, $(\text{CO})_5\text{MC}(\text{HNR})\text{R}'$, $(\text{CO})_5\text{MC}(\text{N}=\text{CR}_2)\text{R}'$, $(\text{CO})_5\text{MC}(\text{SC}_6\text{H}_5)\text{R}$, and $(\text{CO})_5\text{Cr}-\text{C}(\text{OR})\text{R}'$.

$$\begin{array}{c} \diagup \\ \text{N}(\text{C}_6\text{H}_{12}) \end{array}$$

Structures for the carbene complexes were determined from IR, NMR, and mass spectroscopy data.^{1,14,26-28} For the alkoxy carbene complexes, no strong IR bands were observed in the region 1500-1700 cm^{-1} , indicating they were not complexes containing an acyl ligand; rather, a strong band was found in the 1000-1200 cm^{-1} C-O single bond stretching region, suggesting the carbene formulation.²⁹

X-ray crystal structures³⁰⁻³⁵ have confirmed that the compounds can be viewed as carbenes complexed to transition metals. The metal-carbene carbon bond distance was found to be shorter than that expected for a metal-carbon single bond, indicating partial double bond character. The carbene carbon-hetero atom bond distances were intermediate between carbon-hetero atom single and double bond distances.

To the extent that the carbene carbon-hetero atom bond shows double bond character, there can be hindered rotation about this bond, with the possibility of cis(II) and trans(III) isomers. Hindered rotation has been observed in the IR and NMR spectra of amino carbene complexes;²⁸ moreover, the alkoxy carbene complex (methylmethoxycarbene)pentacarbonylchromium (0) gave a temperature dependent NMR spectrum,³⁶ indicating free rotation at room temperature.



Bonding in carbene complexes involves σ donation of the lone pair on the carbene carbon to the metal, and π backbonding from the metal to the empty p_z orbital on the carbene carbon. There is also an interaction between the lone pair on the hetero atom and the carbene carbon p_z orbital. Carbenes have a higher donor/acceptor ratio than carbon monoxide.^{14,30-33}

The Darensbourgs have calculated carbonyl stretching force constants in pentacarbonyl metal carbene complexes using the Cotton-Kraihanzel approximation,³⁷ and then used Graham's method³⁸ to calculate σ and π parameters. Based on these parameters, they described carbenes as both strong σ donors and π acceptors.³⁹

Transition metal carbene complexes have potential usefulness. They offer a synthetic pathway to aldehydes and ketones.^{14,16} They are stable examples of a type of intermediate proposed for some reactions.⁴⁰ Their existence has been used to reassign a structure in terms of a carbene complex.^{41,42}

Fischer has reported the reaction of chromium hexacarbonyl with diethylamide to form another, new type of carbene complex.⁴³ There should be continued work in the future on transition metal carbene complexes.

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CHROMIUM (III) PHOTOCHEMISTRY

James Eaton

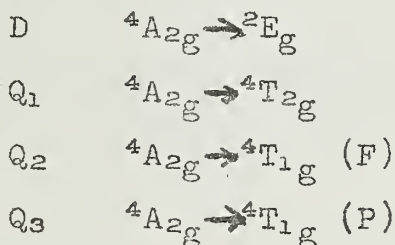
May 20, 1971

Introduction

Chromium (III) photochemistry has been thoroughly investigated, and there is perhaps more information available as to the effects of visible light on these compounds than on any other type of transition metal complex. Chromium (III) photochemistry is particularly simple in that only substitution reactions (i.e., racemization, solvation and isomerization) are observed. The purpose of this seminar will be to discuss the physical aspects of chromium (III) photochemistry and present some representative reactions to indicate how the photochemistry of chromium (III) is different from the thermal chemistry of chromium (III). Using the data resultant from the study of various reactions, the arguments for all proposed mechanisms will be presented.

Background

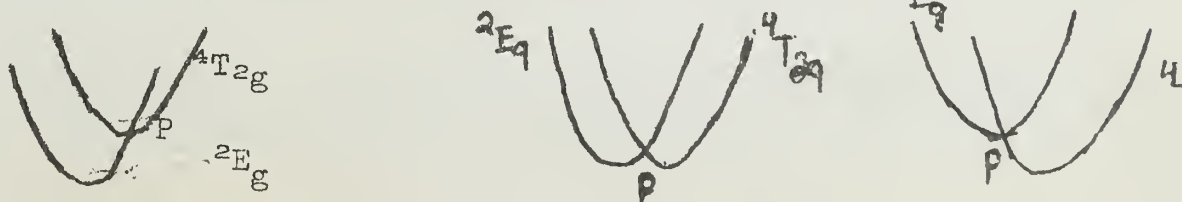
Chromium (III) complexes of octahedral symmetry usually exhibit three ultraviolet bands between 300 mμ and 550 mμ with ε between 10 and 100 and one band 650 mμ and 750 mμ with ε equal to ~1. The stronger bands are designated Q₁, Q₂, and Q₃, with Q₁ being the lowest in energy.¹ The weak band of lowest energy is designated D. They correspond to the following transitions in the molecule:²



In non-octahedral molecules, such as those with C_{4v} symmetry, splitting of these levels may occur. However, if the microsymmetry of the molecule is octahedral, or the ligands fall close to one another in the spectrochemical series, then an octahedral environment is assumed. In molecules which do not fit these classifications, the above symbols are still used, although in a more general sense.

The two states which are important in chromium (III) photochemistry are the ²E_g and the ⁴T_{2g}. It is important to establish their relative positions and lifetimes.

Three possible alignments exist for the ²E_g and the ⁴T_{2g}. These are shown below.³



In figure (a), point p lies at higher energy than the minimum for the doublet state; thus, most of the molecules will cascade down and end up in the doublet excited state where they can phosphoresce to the ground state. In figure (b), both phosphorescence and fluorescence should be observed as both states are equally probable and, in figure (c), only fluorescence should be seen.

From luminescence studies of chromium (III) complexes in rigid glass mediums, all complexes except $\text{Cr}(\text{urea})_3^{+3}$ were found to show phosphorescence only, while $\text{Cr}(\text{urea})_3^{+3}$ shows both. From this and the above discussion, one concludes that the doublet lies below the quartet. Unfortunately, it is dangerous to extend this to non-octahedral complexes as we shall see.

The lifetime of the doublet state has been estimated from phosphorescent emission in rigid glass solution to be on the order of 10^{-9} seconds.⁴ Since no phosphorescent emission is observed at room temperature, the lifetime may be as long as one second. On the other hand, calculations for the lifetime of the $^4\text{T}_{2g}$ state have been reported to give values of about 10^{-8} seconds. Recently, Adamson has presented an article which refutes this. He has shown that a more careful examination of the system leads to the conclusion that the lifetime may be on the order of 10^{-5} seconds. This is important, as some reactions have been reported with activation energies as high as 10 kcals. For this type of reaction, the reactive state must have a lifetime of at least 10^{-6} seconds.

The two higher quartets deactivate quite rapidly to the first excited quartet or to the doublet. Their lifetimes have been estimated at 10^{-11} seconds. This rules them out as possible reactive intermediates.

Reactions

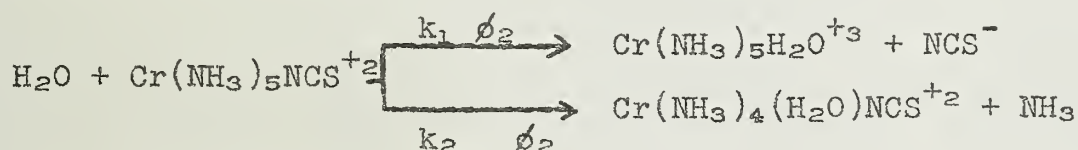
For octahedral complexes, the most studied system is the $\text{Cr}(\text{NH}_3)_n(\text{H}_2\text{O})_{6-n}$. Plane^{6,7} and his group followed the photoexchange of $\text{Cr}(\text{H}_2\text{O})_6^{+3}$ with solvent water by O^{18} tracer. The irradiation was performed in all three bands, Q_1 , Q_2 , Q_3 , and at 0, 10 and 27°C. Unfortunately, the quantum yield was affected by a large experimental error due to the fact that the dark reaction proceeds at a faster rate than the photochemical one.

At 27°C, the quantum yield was reported as 0.02. There is some temperature dependence between 0°C and 10°C, but none between 10°C and 27°C. From this temperature dependence, an E_a of 13 kcals was inferred. This indicates a long lived intermediate, i.e., the $^2\text{E}_g$ state; however, the experimental uncertainty makes this number at least suspect.

For $\text{Cr}(\text{NH}_3)_6^{+3}$ ^{7,8,9} and the other compounds containing mixed aquo-ammonia coordination, the reaction was followed spectrophotometrically. The quantum yield for the irradiation of the three Q

bands was independent of the light intensity and the temperature and was about ten times as large as for the pure aquo complex. Also, the irradiation was performed in the region of the D band, but no increase in quantum yield was noted. The apparent E_a for the reaction was 0.

The photochemistry of many non-octahedral complexes like $\text{Cr}(\text{NH}_3)_5\text{NCS}^{+2}$ and $\text{Cr}(\text{en})_2(\text{OH})_2^+$ have been investigated. They have provided additional information for the determination of a mechanism. However, they have raised as many questions as they have answered. $\text{Cr}(\text{NH}_3)_5\text{NCS}^{+2}$ ^{10,11} undergoes NCS aqutation in the dark. Adamson and Sporer report the photochemical aqutation with a quantum yield of about .07. Later, Waggener found evidence for aqutation of both NCS and NH_3 . Adamson¹¹ did a detailed study on both the thermal and photochemical reactions.



He found that the ratio of k_1/k_2 has an upper limit of .5. The ϕ_1/ϕ_2 ratio was 20 for irradiation in the Q_1 band and 8 for the D band. The quantum yield for the quartet was higher than that of the doublet and essentially temperature independent. The product obtained for the NH_3 aqutation was the trans isomer.

The last reaction of interest is that of $\text{Cr}(\text{en})_2(\text{OH})_2^+$.¹² Thermally both the cis and trans isomers undergo isomerization. However, photochemically the trans species was prone to isomerize, while the cis species underwent aqutation. Thus, it appears that not one, but perhaps two, species are acting as reactive intermediates with their own inherent stereospecificity.

Mechanisms

In general, two mechanisms have been proposed for the photochemistry of chromium (III). The first, which was suggested by Plane^{6,9} and Schl fer,¹³ assumes that regardless of which band is irradiated, the complex terminates in the 2E_g state. For octahedral complexes, this argument has some weight and is accepted by many authors. However, the stereospecificity of non-octahedral complexes has raised some question as to its validity.

In the octahedral complexes, it was noted that regardless of which quartet band was excited, the quantum yield was always about the same. Since it was generally agreed that the higher quartet states deactivated to the $^4T_{2g}$ quite rapidly, and a facile intersystem crossing mechanism did exist from luminescence experiments, then, either the $^4T_{2g}$ or the 2E_g could be considered as the reactive intermediate. The 2E_g being the longer lived of the two was chosen. It was also shown that as the energy separation between

the doublet and the quartet increased, the quantum yield did also. This indicates that thermal population back into the quartet from the doublet has been reduced and more molecules are able to react.

One problem with this is the lack of an increase in the quantum yield upon irradiation of the D band. This is explained by assuming the yield for intersystem crossing from the quartet to the doublet is unity and the reaction competes with deactivation to the ground state.¹⁴

For non-octahedral complexes, however, this mechanism is not enough. In mixed ligand complexes, two photochemical reactions usually occur with the ratio of their quantum yields being wavelength dependent. Several views have been presented to explain this problem. Adamson^{5,8} proposes that the two reactive states are the two lowest quartet states. Wasgestin and Schl  fer¹⁵ indicate in their work with $\text{Cr}(\text{NH}_3)_5\text{Cl}^{+2}$ that the NH_3 release is due to the doublet state and the Cl^- release is due to the charge transfer state. Unfortunately, not enough work has been done to reach any definite conclusions and, until more precise quantum yield and activation studies are undertaken, this question will remain open.

Once the reactive species are determined, mechanistic information will be readily available by comparison with other systems. The $^2\text{E}_g$ state has a vacant t_{2g} orbital and could be compared to the V(III)^g or the Cr(IV) systems, both of which are labile. The $^4\text{T}_{2g}$ has an e_g orbital which is half filled and analogies could be drawn^g between that and the $d^4 \text{Mn(III)}$ system.

Future Directions

Better actinometers and more precise quantum yield measurements are needed to clarify the glaring discrepancies in the already existing data. Also, the area of photosensitizers, as yet untouched, should be explored as precise information on excited states would be provided.

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STUDIES ON LEWIS-ACID-BASE ADDUCTS
(THESIS REPORT)

Thomas O. Maier

May 25, 1971

Introduction

Spectrophotometric measurements have long been used to determine formation constants. For those situations in which the spectrum for each of the absorbing species is not known, various graphical techniques have been used to determine simultaneously the formation constants and molar absorptivities.¹ In the course of investigating 1:1 adducts, it was shown that quite serious errors could be introduced into the resulting data by using standard procedures for calculating these quantities. A rigorous procedure for calculating the data was presented,² but the problem of determining the best solution to the multiple sets of experimental data remained. With the popularization of high speed computers, graphical techniques for finding the best solution have been replaced by numerical search³ or least-squares⁴ techniques. A minimum seeking routine and sharpness of fit criterion for the analysis of 1:1 adducts has previously been described.

Discussion

I have been interested in transition metal ion systems involving both 2:1 and 1:1 adducts. Therefore, I examined possible pitfalls in obtaining and calculating data on these systems. The magnitude of the error that can be introduced by non-rigorous calculational procedures is amazing. Evidently, the source of the error can come from any of three areas: the computer program itself, the accuracy of the spectrophotometric data, and the ingenuity of the experimenter in obtaining his data.

It has been found that for equilibria involving 2:1 adducts, numerical search procedures may fail to find the best set of constants and instead find a local minimum, which appears to be the best fit. The non-linear least squares technique, which varies all adjustable parameters simultaneously, appears to find the true minimum in all cases.

Even though the comparison between calculated and observed data is very small, large uncertainties may be present in the calculated thermodynamic constants.^{4,5} This is usually due to dependence of one variable on another, such that a change in the one can be corrected by a change in the other. The correlation coefficients can indicate when this is a problem. This problem is especially common if $K_2 \gg K_1$.

In using a limited number of data points at a limited number of wavelengths, the selection of data used will often determine the accuracy of the results. Use of concentrations of acid and

base which do not accurately determine all the thermodynamic constants will obviously lead to poor results, but in some cases, this error is not obvious, so the calculated constants may have errors larger than the constants themselves.

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NMR STUDIES OF HALOMETHYLATOBIS(DIMETHYLGLYOXIMATO)-
COBALT(III) ADDUCTS
(Thesis Report)

Raymond S. Stewart

May 27, 1971

The use of inorganic complexes as models for biochemical systems is well established.^{1,2} One particular class of transition metal complexes, methylatobis(dimethylglyoximato)-cobalt(III) adducts, or "cobaloximes," has provided interesting analogies to Vitamin B₁₂.³ Although many cobaloximes have been synthesized, there have been few reported effects to evaluate quantitatively the reaction of these compounds in solution.

One particularly attractive method for systematically attacking this problem has been to study the ligand exchange properties of cobaloximes. Although various spectroscopic tools have been utilized, one recent report used proton nmr.⁴ The rates of ligand exchange were shown to be on the nmr time scale and a relative ordering of several Lewis bases was reported.

Recent studies by Wood and coworkers have included the syntheses and characterization of halomethylcobalamins.^{5,6} The reactivity of these Vitamin B₁₂ derivatives suggest a dependence on the electronegativity of the halomethyl moiety. It was therefore decided to attempt to carry out studies on suitable analogous cobaloximes. Today's seminar will deal with the synthesis and proton nmr studies of halomethylcobaloximes.

Monohalomethyl- and dihalomethylcobaloximes were synthesized using routine procedures.⁷ Serious difficulties arose in the attempted preparation of trihalomethylcobaloximes. These difficulties will be discussed and contrasted with the successful syntheses of trihalomethylcobalamins.

A general two-site computer program⁸ was used to evaluate the variable temperature nmr data for several halomethylcobaloximes. Where quantitative studies could not be done, the qualitative results will be discussed. The kinetic data will be compared with recent results obtained for other cobaloximes.

Several trends are suggested from the data and these will be discussed and contrasted with the reported trends in halomethylcobalamins.

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STRUCTURAL AND CHEMICAL INVESTIGATIONS OF SOME ORGANIC AND ORGANOMETALLIC MOLECULES

(THESIS REPORT)

James S. Swanson

June 1, 1971

Thesis research was conducted in four distinct areas. These areas may be categorized as follows: 1. Structural and chemical investigations of compounds containing three membered heterocyclic rings. 2. Synthetic and mechanistic studies of systems involving reactions between nickel carbonyl and chloroolefins. 3. Structural investigations of several cobaloxime complexes which have been proposed as Vitamin B₁₂ models. 4. Structural study of tetramethylammonium chloride hydrogenchloride aimed at elucidating the special features of the Cl-H-Cl hydrogen bonded anion. A brief review of these problems follows.

1. This problem, originally scheduled to be a joint study of the bonding electron density in tetracyanoethylene oxide utilizing X-ray and neutron diffraction data, has taken two directions. The results of the X-ray and neutron diffraction studies are completed¹ and were first reported in a paper given at the Winter A.C.A. Meeting in New Orleans (Abst. K6, March 4, 1970). My main contribution to this problem involved the preparation of suitable crystals for both the X-ray and neutron diffraction experiments, carrying out the initial X-ray investigation and acquiring supporting data such as mass spectra and infrared. While attempting to synthesize other suitable three membered heterocyclic ring systems to study, a thorough investigation of published procedures for diaziridine syntheses was made. During this synthetic study, the bisulfate salt of dimethyldiaziridine was isolated and characterized.² Dimethyldiaziridine was synthesized utilizing known procedures which had not previously been tried, and spectral data was obtained which strongly indicated that a new compound, dicyanodiaziridine, had been formed in another reaction. A preliminary single crystal X-ray investigation of dimethyldiaziridine was also made.

2. Olefins are known to undergo specific reactions in the presence of Ni(CO)₄, which depend on the reaction conditions employed.³ These reactions include carboxylation, acylation, dimerization and complex formation. Mechanisms for each type have been postulated in the literature. It has been observed, however, that "activated" olefins such as acrylonitrile, 1,1-dicyano, 1,1,2-tricyano, and tetracyanoethylenes are unreactive to carbonylation,⁴ and generally unpredictable in their reactions with Ni(CO)₄.⁵ A perusal of the recent literature suggests that, with the exception of platinum and palladium, the reactions between highly chlorosubstituted olefins and transition metals have been neglected. In those systems which have been examined, oxidative addition reactions are generally found to occur in the presence of low valent metals.⁶

These data suggest that "activated" olefins behave differently in their reactions with $\text{Ni}(\text{CO})_4$ than their mono- or unsubstituted analogs. We have studied the reactions of pentachloropropene (PCP), tetrachlorocyclopropene, chloroacrylonitrile, and α,β -dichloroacrylic acid in the presence of $\text{Ni}(\text{CO})_4$ and found that dimerizations, polymerizations, and carbonylations can occur. Organic reaction products were characterized by i.r., n.m.r., and mass spectroscopy, along with elemental analyses. The isolation of nickel-chloroolefin adducts and CO evolution measurements suggest mechanistic differences in the reactions involving chloroolefins.

3. Single crystal X-ray diffraction studies have been carried out on several cobaloxime complexes, $[\text{CH}_3\text{Co}(\text{DH})_2\text{L}]$; $\text{L} = -\text{CNCH}_3$, $\text{P}(\text{OCH}_3)_3$, and $(\text{CH}_3\text{Co}(\text{DH}_2)_2)_2$, which have been proposed as models for Vitamin B_{12} . To date, the crystal structures of methylato bisdimethylglyoximate Cobalt(III), a dimer and methylatotrimethylphosphato bisdimethylglyoximate Cobalt(III) have been solved and a preliminary X-ray investigation of the methylisocyanide analog has been completed. This work has been carried out in collaboration with Dr. T. L. Brown's group, who have prepared the compounds and studied their chemistry by spectroscopic techniques,⁷ including n.m.r., i.r., and n.q.r. The structural studies may prove to be invaluable aids in a more complete understanding of these model systems.

4. This was also a collaborative project carried out during the Summer of 1969 at Argonne National Laboratory under the supervision of Dr. Jack Williams. A survey of the recent literature regarding salts thought to contain the bichloride ion $(\text{Cl}-\text{H}-\text{Cl})^-$ revealed considerable controversy regarding both the geometry of the anion in the tetramethylammonium salt and the nature of the hydrogen bond present.⁸ We investigated the structure of this compound by single crystal X-ray diffraction methods. The results⁹ indicated the presence of an asymmetrical hydrogen bond, which was subsequently proven by a neutron diffraction study.¹⁰

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VIBRATIONAL SPECTRA AND BONDING IN PLATINUM(IV) CYANIDE COMPLEXES (THESIS REPORT)

Mel Memering

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Introduction

In contrast to the numerous vibrational studies of substituted metal carbonyls, comparatively few vibrational studies have focused on the analogous cyano metal complexes. Vibrational studies of mono-substituted metal cyanides have been limited mainly to pentacyano-nitrosyls.¹ In addition, most of these studies have been restricted to the C-N stretching region.

This thesis report will discuss the vibrational spectra and bonding for the series of complexes $M_2Pt(CN)_5X$ (M = alkali metal; $X = Cl, Br, I, CN$). This system is interesting in that σ -bonding predominates over π -bonding because of the large effective nuclear charge of platinum(IV).

Synthetic Procedures

Preparation of $K_2Pt(CN)_5I$ involved the method of Babkov² in which $K_2Pt(CN)_4$ is oxidized by cyanogen iodide. The bromo and chloro species were prepared by an in situ oxidation of the iodide by the respective halogen;³ the hexacyano complex, by cyanide substitution of the iodo complex.² The salts of the other alkali metals were prepared in an analogous fashion or by metathetical processes. Exchange reactions with isotopically labeled KCN(60% ^{15}N) were also attempted to test the feasibility of stereospecific substitution.

Analysis of Vibrational Spectra

Infrared intensity measurements in the cyanide region indicate that the extent of π -bonding in this system is comparatively small.⁴ The effect of the halide is small, but measurable; the amount of π -bonding increases in the order $Cl < Br < I$.

There are a number of factors which affect the position of cyanide stretching frequencies. In simple non-bridging cyanide, ν_{CN} falls within a narrow range defined by the ratio of coordination number to oxidation state of the central metal.⁵ When bridging or strong cationic attractions take place, the cyanide stretching modes invariably are shifted to higher energies.^{6,7} The large shifts observed in the formation of adduct bands result from a change in cyanide force constants;⁸ small shifts due to lattice interaction can be attributed simply to a change in the mechanics of vibration in this system.⁹ These interaction effects are demonstrated by a number of hexacyanoplatinate(IV) salts.

Unambiguous assignments of skeletal C-N and Pt-X stretching modes were obtained, though the exact position of the apical A_1 stretching vibration could not be determined with accuracy. The

C-Pt-C and C-Pt-X deformations as well as lattice modes can be assigned for the regions below 200 cm^{-1} .

Since no less than ten fundamental modes are expected in the region $500\text{-}300\text{ cm}^{-1}$, spectra in this region are quite complicated by coupling, lattice interactions, and the effect of the halide substituent. The assignments postulated for this region should be regarded as tentative at this point.

Conclusion

Because of the high degree of σ -bonding exhibited in these complexes, a number of interesting phenomena are observed:

- (1) The extent of π -bonding is minimal.
- (2) The positions of cyanide absorptions occur at very high energies, especially in bridging systems.
- (3) The nature of the halide substituent has little effect on the vibrational spectra of the complexes.
- (4) By comparison with the effect of halide on the vibrational spectra and bonding, intermolecular lattice interactions are dominant.

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